

SOUTHERN LAKE HURON:
HYDROCARBONS AND FATTY ACIDS IN SEDIMENTS

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ABSTRACT

The amounts and types of hydrocarbons and fatty acids in sediments at eight locations in southern Lake Huron and four locations in Saginaw Bay have been determined. Saturated hydrocarbons appear to be sufficiently resistant to alteration over at least 11,000 years to be used to characterize past sources of organic material to lake sediments. Fatty acids and unsaturated hydrocarbons are subject to alteration and seem to be primarily the *in situ* products of benthic communities, although a portion of the fatty acids may be derived from allochthonous sources. Changes in hydrocarbon composition with depth in Saginaw Bay sediments gives evidence of increasing eutrophication of the overlying waters over the past 40 years and of deforestation of the Saginaw Bay watershed 100 to 120 years ago. Variations in hydrocarbon and fatty acid content of cores from Lake Huron suggest natural variations in both watershed and autochthonous populations of organisms which predate European settlement of the Great Lakes Basin.

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SECTION 1

INTRODUCTION

An important aspect of biogeochemical investigations is to provide information about the sources of organic matter contained within sediments. Most studies of this nature have investigated ancient sediments with the goal of characterizing the organic sources in prehistoric depositional environments. However, it is useful to study the contemporary organic geochemistry of sedimentary environments in order to contribute to a better understanding of materials found in ancient sediments. Furthermore, organic matter in modern sediments is not far removed, if at all, from biological processes and is therefore important for ecological reasons.

A portion of the organic materials biosynthesized by aquatic organisms is incorporated into underlying sediments. Additional organic matter is contributed by benthic organisms, and more is carried to the sediments with land-derived sedimentary materials. While most of the organic carbon content of sediments is found in amorphous polymeric materials which are not easily isolated, a small, extractable fraction comprised of identifiable classes of compounds always exists.

Among these classes, lipid matter, or that class of compounds extractable with organic solvents, is particularly important. These lipids include fatty acids and their esters, fatty alcohols, and hydrocarbons. Their geochemical importance is derived from their carbon skeletons which can be preserved over long periods of geological time although the structure of the molecule may be modified. Thus, the preserved carbon skeleton serves as a clue to the biologically synthesized precursor of the geolipid, and the structural modification suggests the type of geochemical processes the molecule has experienced.

LITERATURE REVIEW

Many investigators have analyzed geolipids in sediments, and a number of reviews of the resulting data have been published (Breger, 1966; Kvenvolden, 1967; Eglington, 1968; Meinschein, 1969; Parker, 1969; Maxwell, *et al.*, 1971; Cranwell, 1975; Morris and Culkin, 1975; Seifert, 1975, Farrington and Meyers, 1975; Barnes and Barnes, 1978). From these data, it is evident that geolipids are subject to alteration over geologically long time spans. Furthermore, some types of lipids become altered more than others. It is also evident that most investigators have studied ancient geological deposits in which the early stages of alteration have long since occurred. However, a limited number of reports exist which describe the early modifications of geolipids in Holocene sediments.

Fatty acids, in particular, appear to be relatively reactive in modern sedimentary environments. Parker (1967), in his report of fatty acid compositions in sediments from six different marine locations, concludes that "Much of the geochemical modification of fatty acids takes place early." He found total acid concentrations decreased to levels similar to those of ancient sediments and amounts of unsaturated compounds dropped rapidly with depth. The loss of unsaturation can be partially explained by reduction of double bonds, but because branched-chain acids became more abundant with depth, processes more complex than simple destruction or reduction must be contributing to the observed modifications. As examples of some other possible alterations which fatty acids undergo, Van Vleet and Quinn (1976) suggest that conversion of cis configuration to trans configuration and migration of double bonds can occur in olefinic acids in young sediments.

As part of an extensive survey of sediment geolipids in a New England estuary, Farrington and Quinn (1971a) found fatty acid distributions similar to those reported by Parker (1967). Total fatty acid levels decreased with depth, and the rate of decrease was greater for unsaturated than for saturated acids. Although there were variations in types and amounts of fatty acids at different locations in the estuary, there appeared to be no temporal variations at one location over a one-year period (Farrington and Quinn, 1973a). In a similar but independent study of Holocene sediments from a British Columbia fjord, Brown *et al.*, 1972, also found that saturated and total fatty acid levels decreased with depth. They concluded that these changes were post-depositional effects, because the ratio of fatty acids to total organic carbon also decreased. However, Farrington *et al.* (1977) found the levels of total acids and of total organic carbon to decrease together, at a constant ratio, with depth in a coastal marine sediment. Apparently, variations in types and amounts of fatty acids and also in diagenetic processes are found in different depositional environments, and inconsistencies such as this call for further investigation.

The question of the fate of unsaturated fatty acids in young sediments has been partially answered by Rhead *et al.* (1972). They found that about 2 percent of oleic acid was converted to saturated acids of various chain lengths after only a few days' incubation in estuarine muds. The other 98 percent was altered to more polar geolipids or became non-lipid material. Based upon this experiment, these investigators concluded that many of the fatty acids found in modern and ancient sediments are not originally included in sedimented organic matter, but are derived from it via various conversion processes (Rhead *et al.*, 1971). However, it is possible that fatty acids are rapidly incorporated into humic substances in recent sediments inasmuch as fatty acids have been shown to be major components of soil humic and fulvic acids (Schnitzer, 1976). Over geologic time, a portion may be recycled to a more easily extractable form in ancient sediments.

Johnson and Calder (1973) showed that plant-produced fatty acids in salt marsh sediments experienced a loss of unsaturated and a gain of branched components in both oxidizing and reducing areas. Measurement of ^{13}C indicated neither much horizontal movement of geolipids nor additional isotope fractionation during the alteration stages. In a similar study, Sassen (1977a, 1977b) found that a portion of mangrove fatty acids were preserved in underlying sediments. Again, levels of unsaturated components decreased while branched components increased with depth. A source of iso- and anteiso-fatty acids is bacteria. Therefore, detection of branched fatty acids is indicative

of microbial activity in sediments (Parker, 1967; Cooper and Blumer, 1968; Brooks *et al.*, 1977). The importance of microbial contributions to the geolipid content of surficial sediments is stressed by Boon *et al.*, (1975), who conclude from their analysis of a continental shelf marine sediment that a large portion of the total fatty acids is derived from bacterial synthesis at the sediment surface.

From a survey of fatty acids in the sediments of English lakes, Cranwell (1974) concluded that the concentration of the branched and cyclic saturated acid fraction correlates directly with the productivity of lake surface waters and can be used as a paleolimnetic indicator. At the same time, chain-length distributions of n-alkanoic acids can record the relative contributions of aquatic versus land sources of sediment organic matter. Also, it appeared that fatty acid alteration and destruction were retarded in lakes having high sedimentation rates.

Fatty alcohols are also found in the lipid extracts of Holocene sediments. Sever and Parker (1969) found total fatty alcohol levels in a number of marine sediments to be the same as or only one order of magnitude less than concentrations of total fatty acids. This is surprising, since fatty alcohols are usually present in living systems at levels several orders of magnitude lower than those of acids. Also, dihydrophytol was found in all the sediments investigated. This alcohol is rare in organisms, but probably can be derived from chlorophyll under anoxic conditions in sediment by reduction of the phytol side chain. Although modification of alcohols evidently can occur in sediments, certain compounds may be useful geochemical indicators over periods of many thousands of years.

Sterols, in particular, have been suggested as potential indicators of source materials and diagenetic processes and have been detected in modern marine sediments (Attaway and Parker, 1970). Recently, Huang and Meinschein (1976) identified a systematic shift in the ratio of cholesterol to -sitosterol in sediments with change from riverine to marine conditions. This shift correlated with similar changes in sterol compositions of mixed plankton samples from the overlying water, showing that sterols could be good indicators of source materials in sediments. Two sources were identified in this study -- terrigenous and marine planktonic. A third source -- marine benthic -- has been indicated by a study of samples of Buzzards' Bay sediments by Lee *et al.* (1977). This study also showed that sterol concentrations decrease over time periods as short as 120 years via conversion and decomposition processes, although not as quickly as fatty acid concentrations. One type of conversion process which occurs and which would act to stabilize the carbon skeleton of sterols is hydrogenation. Increases in stanol-stenol ratios have been found with depth in sediments from Rostherne Mere, England, (Gaskell and Eglinton, 1976) and Lake Suwa, Japan, (Nishimura and Koyama, 1976, 1977). As in previous studies, these three investigations also noted evidence of variations in source materials as indicated by sterol compositions.

Hydrocarbons appear to be the class of geolipids, and indeed of organic matter in general, most resistant to alteration in sediments. This characteristic has enabled researchers to utilize hydrocarbon patterns as another indicator of sources of lipid input over Holocene history. Using distributions of normal alkanes found in the sediments of English lakes, Cranwell (1973) was able to deduce changes in the vegetations of the drainage basins serving these lakes. Gaskell *et al.* (1975) employed patterns of normal alkanes plus those of fatty acids to assess the relative contributions of

marine versus terrestrial sources of organic matter in a core representing 10,000 years of sedimentary history from the continental shelf off northwest Africa. They found organic matter to be particularly well preserved in this sediment sample, indicating low *in situ* microbial activity. In contrast, Johnson and Calder (1973) found major changes in sediment lipids due to microbial activity in a tidal marsh environment. Hydrocarbon distribution patterns rapidly changed with depth, although at a slower rate than those of fatty acids. Evidently, the characteristics of different depositional environments lead to different combinations of alteration and preservation of geolipids.

Distributions of aliphatic hydrocarbons in surficial sediments have been used to identify possible origins of these geolipids. Ratios of odd-to-even normal alkanes found in Beaufort Sea sediments suggest that nearshore sediments contain organic matter originating primarily from land, while offshore sediments have a predominantly marine source of organic matter (Peake, *et al.*, 1972). In a comparative study of sediment samples collected at 60 locations in the northeast Gulf of Mexico, Gearing *et al.* (1976) were able to identify two distinct continental shelf environments on the basis of aliphatic hydrocarbons. The first had low levels of hydrocarbons which were dominated by n-heptadecane, characteristic of marine algae. This environment, off central Florida, appeared to have a primarily marine source of hydrocarbons. The second region had higher levels which were dominated by C₂₇, C₂₉, and C₃₁ n-alkanes, representative of vascular plants. This environment, closer to the Mississippi River, seemed to be dominated by land-derived hydrocarbons. Furthermore, hydrocarbon patterns from this area contained fairly conspicuous unresolved complex mixtures of aliphatics. Because such mixtures are indicative of petroleum hydrocarbons, a fossil fuel origin of a portion of the hydrocarbons in this second area is suggested.

This observation points out a useful practical application of determining hydrocarbon distribution patterns in sediments -- that of identifying and quantifying petroleum contamination. This approach has been used in a New England estuary by Farrington and Quinn (1973b) to detect a sediment contamination gradient decreasing from Providence, R.I., to the mouth of the bay. Using this approach, Palacas *et al.* (1976) examined nearshore sediments from a variety of northeast Gulf of Mexico locations and found them to be free of obvious petroleum contamination.

Recently, Wakeham and Carpenter (1976) and Wakeham (1977) reported some of the results of an extensive study into the hydrocarbon composition of sediments from Lake Washington. They find surface sediment aliphatic hydrocarbons similar to those found in petroleum. The contribution of this mixture to total aliphatics decreases with depth in the sediment until, at a depth corresponding to an age of about 100 years, it virtually disappears. In sediments older than this, the composition is dominated by normal alkanes in the C₂₁ to C₃₁ range. A possible explanation of this distributional pattern is that the advent and continued use of petroleum hydrocarbons beginning about a century ago is recorded in these sediments. This conclusion is verified by radiocarbon ages of surficial sediment organic matter which are greater than those of deeper sediment organic matter and by comparison of Lake Washington hydrocarbon distributions to those from a pristine lake (Wakeham, 1976).

In a study particularly pertinent to this project, Reed (1977) examined the lipid content of sediments from Mono Lake, California. Differences in n-alkane and sterol distributions were found between near-shore and deep-basin

locations which could be attributed to source materials, even though evidence of alteration of lipid components existed. Variations in n-alkane and sterol distributions with depth in these sediments can be used to identify periods of eutrophy and oligotrophy in the Pleistocene history of this lake (Reed, 1976). Correlation of variations of several classes of geolipids provides good support for the paleolimnetic interpretations made by Reed.

From these reports, it is evident the different classes of components comprising geolipids undergo alterations in Holocene sediments to varying degrees and at different rates. Although the products of such alterations are not well-studied, it is evident that a certain amount of interconversion occurs between the lipid classes (Kvenvolden, 1967; Eglinton, 1968; Maxwell *et al.*, 1971; Rhead *et al.*, 1971). For this reason, the study of several lipid classes coexisting in a sediment seems potentially more productive than the study of a single class. To date, only a limited number of investigators have reported such studies in Recent sediments (Brown *et al.*, 1972; Peake *et al.*, 1972; Farrington, 1972, Johnson and Calder, 1973; Gaskell *et al.*, 1975; Brooks *et al.*, 1976, 1977; Reed, 1977; Cranwell, 1978).

OBJECTIVES

In view of the findings of previous studies of lipids in sediments it was decided that an investigation providing a number of comparisons of fatty acid and hydrocarbon distributions in surface sediments would provide better information about sources of these materials and about processes active in altering organic compounds near the sediment-water interface. Comparison of these distributions at different depths in the sediment column would yield information about changes in the depositional environment over modern time and perhaps about slower-acting alteration processes.

Better knowledge of the modifications which natural geolipids have undergone would be useful in projecting the short-term and long-term fates of both natural and anthropogenic lipids added to modern sediments in general. Furthermore, because nearly all studies of geolipids have been of the marine environment, more information on freshwater systems would be especially useful to the overall field of organic geochemistry.

Therefore, this investigation was undertaken with the primary objective of identifying changes in the lipid content of Lake Huron sediments which recorded the most recent 300 years of lake history. This was achieved by examining the fatty acid and hydrocarbon content of sediment cores obtained at three selected locations in southern Lake Huron and in Saginaw Bay.

A secondary objective was to determine if differences in organic constituents of surface sediments could be identified between locations close to shore and far from shore. This was done by measuring fatty acids and hydrocarbons in samples obtained from two transects in southern Lake Huron and one transect in Saginaw Bay. This portion of the study provided information concerning the importance of land sources versus lake sources of organic matter to Lake Huron sediments.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The results of this study of geolipids in sediments of southern Lake Huron and Saginaw Bay can be summarized in the following conclusions:

- 1) Fatty acids and resolved hydrocarbons in sediments from twelve locations in Lake Huron give clear evidence of recent biogenic origins. Both aquatic and terrigenous sources are indicated. Dominant fatty acid sources appear to be aquatic and are probably algal and microbial in type whereas n-alkane distributions have a significant terrigenous component. This suggests that the more refractory hydrocarbons experience greater amounts of transport and dispersion than do the more labile fatty acids.
- 2) Sediment geolipid content varies across sedimentary basins. This may be due to changes in sediment texture, patchiness in benthic communities, geochemical microenvironments, variations in source materials, or different transport times and routes. Many of these parameters are interrelated, and their effects cannot be isolated.
- 3) Organic matter from Saginaw Bay sediments differs from that in southern Lake Huron sediments. Much of this difference appears to be a result of increased productivity and biomass in the sediments and waters of Saginaw Bay beginning 100 to 120 years ago.
- 4) Fatty acids in Lake Huron sediments appear to originate largely from the benthic environment. Because these compounds are relatively reactive in sediments, they serve as a measure of alteration processes and rates.
- 5) Saturated hydrocarbons are useful as indicators of sources of organic matter to Great Lakes sediments. They appear to be resistant to alteration for time periods up to 11,000 years.
- 6) Unsaturated and aromatic hydrocarbons are potentially valuable indicators of specific sources of organic matter input to Great Lakes sediments. However, identification of individual components was not possible in this investigation.
- 7) Saginaw Bay surficial sediments appear to receive a significant anthropogenic input of petroleum-derived or industrially produced hydrocarbons, possibly via urban run-off and effluents.

On the basis of this investigation, several recommendations can be made. While many of these involve procedures employed in this study, some suggestions for improving the quality of information which studies such as this can provide are offered. All the recommendations are applicable to future investigations.

1. Several classes of organic compounds, such as fatty acids and

hydrocarbons, should be analyzed in every sample. Data from such an approach provide a total picture which is greater than the sum of its parts.

2. Sediment accumulation rates should be known if information is desired about rates of alteration of organic materials or about the sedimentological record.
3. Sediment texture should be determined. This information permits inferences to be made about sources and histories of sedimentary particles. Also, grainsize is a factor affecting organic and inorganic content of sediments.
4. Extensive analytical surveys of organic constituents in Great Lakes sediments should be discouraged, unless each and every sample can be properly analyzed. It is far more productive to sample a basin selectively and to analyze thoroughly a few sample areas than to amass large amounts of inadequate data.
- 5.. Future studies of organic materials in the Great Lakes should include mass spectrometry as one of the essential analytical methods. However, it is not necessary that every sample in an investigation be analyzed by mass spectrometry.
6. Finally, this study has indicated the usefulness of lipid components as indicators of paleolimnetic processes. It is suggested that further studies of fatty acids and hydrocarbons in Great Lakes sediments be planned. Sterol analyses should be included in future studies, because many of the compounds can be used as biochemical tracers of specific organisms.

SECTION 3

PROCEDURES AND METHODS

SAMPLES

Sediment samples were collected in southern Lake Huron and Saginaw Bay during 1974 and 1975 at locations also sampled by Robbins (in preparation). Locations representative of different bathymetric zones and of different sedimentary regimes as described by Thomas *et al.* (1973) were selected. Table 1 describes sampling locations and sediments from which the data in this report were generated. The locations of the sampling stations in Lake Huron and in Saginaw Bay are shown in Figure 1. Samples in addition to those in Table 1 were collected during 1974 and 1975, but have not been examined and will be preserved for future studies. A tabulation of these additional samples by location and type is given in Appendix I.

Sampling was done with a Benthos 6.6 cm diameter gravity corer equipped with a butyrate liner. Cores were sectioned by a vertical extrusion procedure within an hour of collection. The top 10 cm of a core was divided into 1 cm sections, the 10 to 20 cm portion was divided into 2 cm sections, and the

TABLE 1. SOUTHERN LAKE HURON SEDIMENT SAMPLES

Location	Sample	Type	Water Depth	Surficial Sediment
Goderich Basin:				
43°51'N, 82°05'W	SLH74-12	core	91 m	brown clay-silt
43°25'N, 82°10'W	SLH75-41	surficial	44 m	sand
43°25'N, 82°05'W	SLH75-42	surficial	48 m	brown clay-silt
43°25'N, 81°55'W	SLH75-43	surficial	27 m	brown sandy-silt
43°45'N, 81°55'W	SLH75-54	surficial	42 m	brown silt
43°45'N, 82°05'W	SLH75-55	surficial	86 m	brown silt
43°45'N, 82°10'W	SLH75-56	surficial	55 m	gray sandy silt
43°50'N, 82°00'W	SLH75-58	core	73 m	brown silt
Saginaw Bay:				
43°58'N, 83°37'W	SB75-6A	surficial	12 m	brown-gray clay
43°54'N, 83°40'W	SB75-17A	surficial	11 m	brown-gray clay
43°51'N, 83°43'W	SB75-30A	core	9 m	brown-gray clay
43°47'N, 83°46'W	SB75-42A	surficial	8 m	brown-gray clay

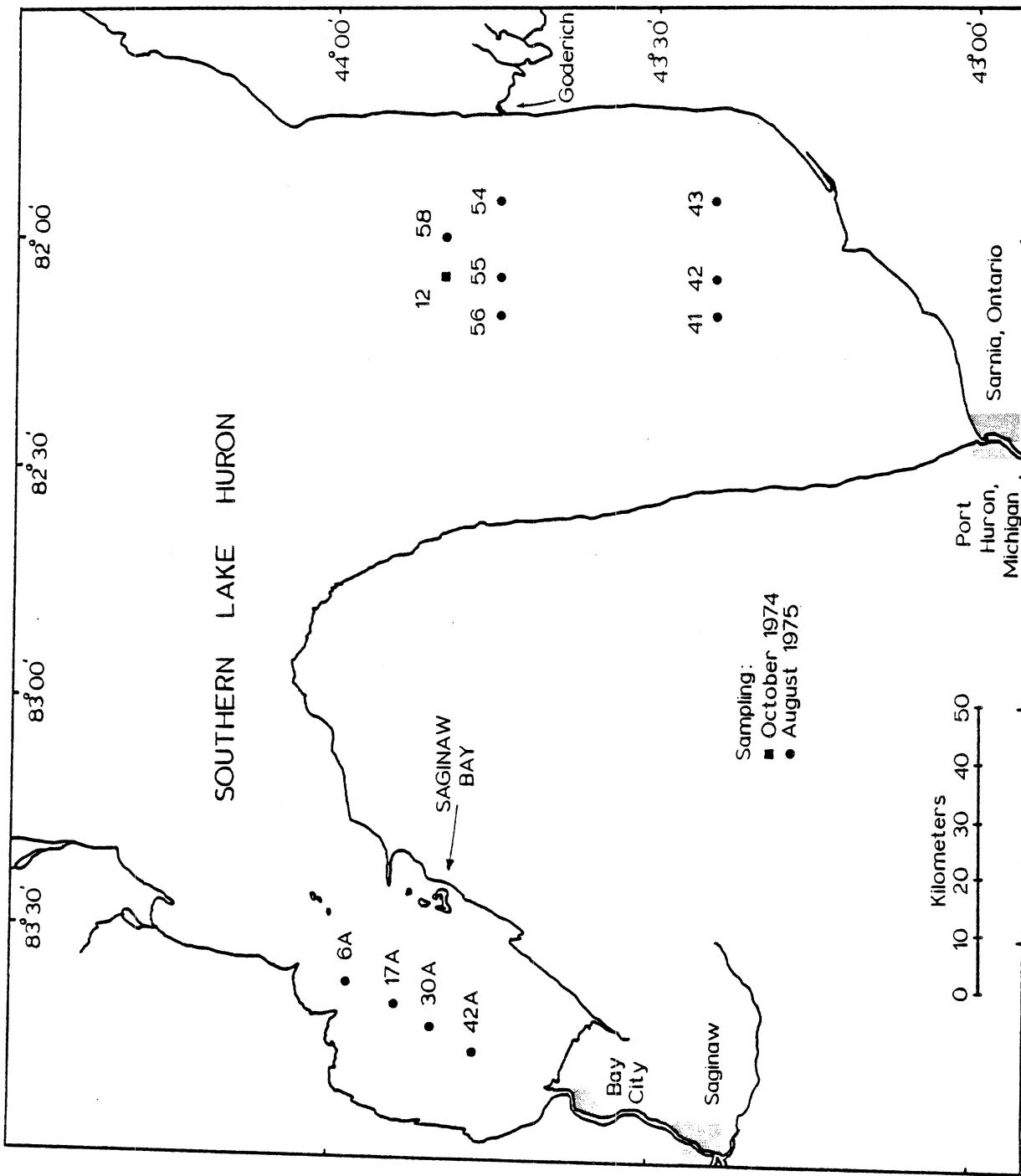


Figure 1. Sediment sampling stations in southern Lake Huron and Saginaw Bay.

portion of the core below 20 cm was divided into 5 cm sections. Surficial sediment samples representing the top 5 cm of sediment were also obtained by coring. Sediment samples were immediately frozen in solvent-rinsed glass jars and maintained at -20°C until analysis.

Modern sedimentation rates have been measured at a number of locations in Lake Huron by J. A. Robbins (in preparation) using ^{210}Pb dating techniques. The sediment accumulation rate at station SLH74-12 is 1.1 mm/yr, and at station SB75-30A it is 2.5 mm/yr. At station SLH75-58, a layer of sand was encountered at a depth of 3 to 5 cm. This suggests loss of modern accumulation by slumping or some other process. Therefore, sedimentation rate determination by ^{210}Pb dating would be meaningless and Robbins made no attempt at this measurement. However, this core provided a valuable contrast to the two uninterrupted cores.

GENERAL ANALYSIS SCHEME

The extraction and analysis procedures employed in this study were developed to provide information about several lipid classes found coexisting in samples of lake sediments. Many of the individual steps have been borrowed from previous studies (e.g., Farrington and Quinn, 1971b; Gearing *et al.*, 1976; Gaskell *et al.*, 1975; Farrington and Tripp, 1975; and Wakeham and Carpenter, 1976). However, the overall analytical approach was specifically designed for this project. It is represented schematically in Figure 2.

TOTAL ORGANIC CARBON

Portions of each sample were dried at $60 + 5^\circ\text{C}$ to constant weight. Carbonate-carbon was removed by treatment with excess 1 N HCl. After being filtered on pre-ignited glass fiber filters and being rinsed with distilled water, the carbonate-free sediment was dried to constant weight and homogenized by crushing with mortar and pestle. The organic carbon content was determined by oxidation at 1100°C in a Hewlett-Packard model 185-B CHN analyzer. Daily calibration curves were made using cystine as a standard. Triplicate analyses on several samples gave an average coefficient of variation of 3.7 percent of the mean.

LIPID EXTRACTION

The wet-sieved (1 mm) sediment was subject to a saponification-extraction adapted from the method recommended by Farrington and Quinn (1971b). The saponification-extraction reagent was a mixture of 0.5 N KOH in 95 percent methanol and benzene in a 2:1 volume ratio. Saponification was achieved by refluxing for one hour using a reagent/wet sediment ratio of about seven volumes of reagent per unit weight of solvent. After cooling, the saponification mixture was filtered through Whatman No. 541 filter paper held in a Buchner funnel and washed three times with benzene:methanol (1:1).

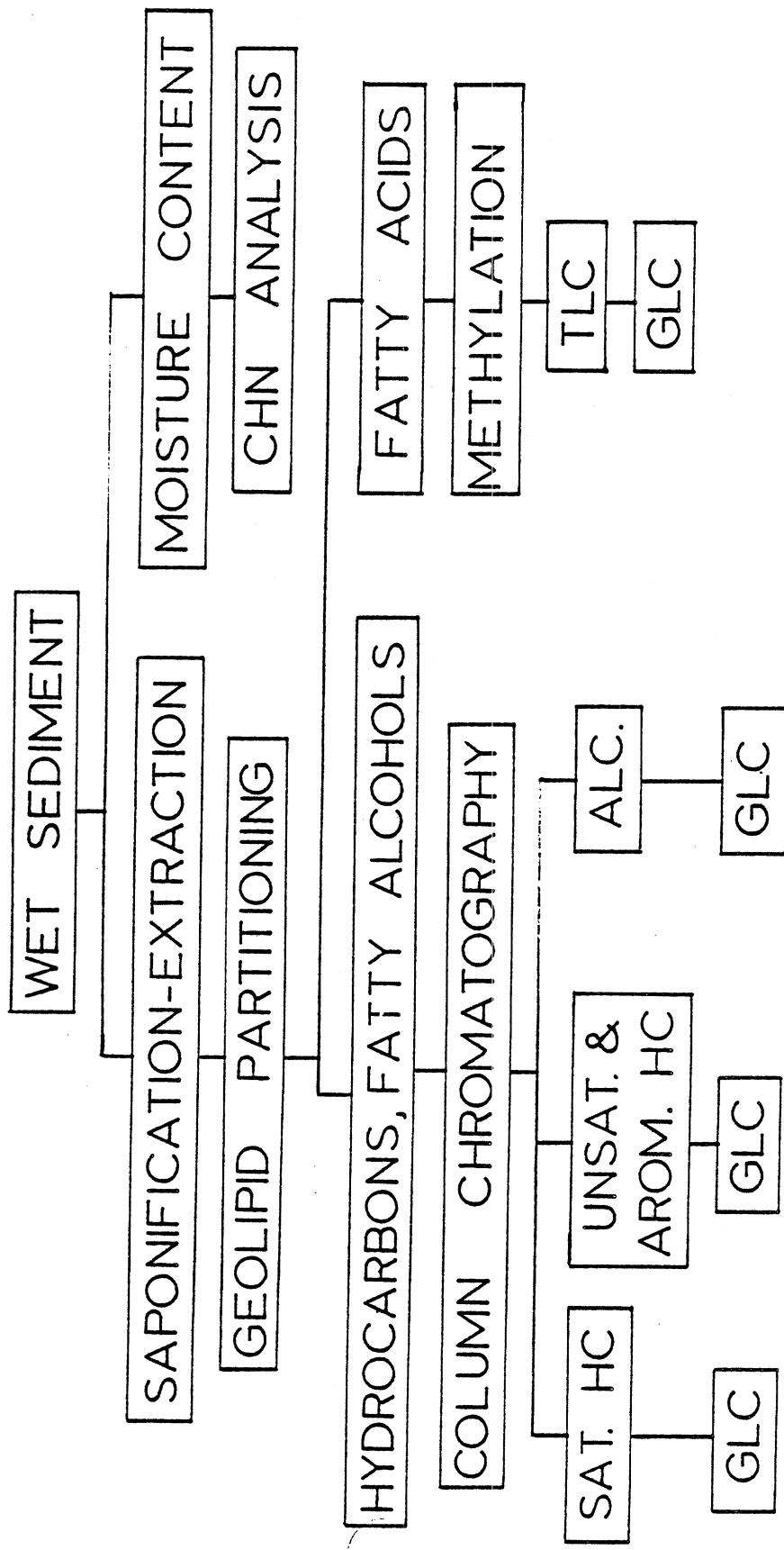


Figure 2. Outline of analytical procedure for sediment organic matter composition.

ISOLATION OF LIPID CLASSES

The combined filtrate and washes from above were transferred to a separatory funnel. A volume of distilled water equal to the saponification-extraction volume of benzene was added to partition the mixture into two phases. The organic phase contained non-polar lipids, and the aqueous/methanol phase ($\text{pH} > 10$) contained polar lipids. The aqueous/methanol phase was re-extracted two times with petroleum ether (b.p. $35.8 - 56.5^\circ\text{C}$); these extracts were combined with the initial organic phase and evaporated to dryness on a rotary evaporator using a water bath temperature of 30°C . The aqueous/methanol phase was retained for fatty acid analysis.

The dried residue of the organic phase was dissolved in benzene:methanol (1:1) and percolated through a 15×1 cm column of copper powder, freshly cleaned with 3 N HCl, to remove any elemental sulfur (Blumer, 1957); no blackening was ever observed. The column eluate was evaporated to dryness.

The non-polar lipids were partitioned into three fractions by column chromatography. The column was made by wet-packing in benzene two grams of aluminum oxide (Neutral, J. T. Baker) over two grams of silica gel (Davison, grade 923, 100-200 mesh). Both adsorbents were prepared by drying for 12 hours at 120°C , followed by deactivation with five percent water. The packed columns were rinsed with several column volumes of petroleum ether-benzene mixtures, gradually increasing the petroleum ether concentration up to 100 percent. The sample was dissolved in chloroform and adsorbed onto 1 gm of aluminum oxide by evaporation on a rotary evaporator. The sample was placed on top of the alumina/silica gel bed by transfer of the 1 gm of aluminum oxide, resulting in a total column height of 8 cm and a height/diameter ratio of 9/1.

The column was eluted with three solvents in increasing order of polarity: first, 10 ml of petroleum ether (PE fraction), next with 14 ml of benzene (BZ fraction), and finally with 25 ml of 9:1 benzene:methanol (BM fraction). The PE fraction contains alkanes, cycloalkanes, and mono-unsaturated alkanes. Polyunsaturated alkenes, aromatic hydrocarbons, and ketones are contained in the BZ fraction. In the BM fraction are found alcohols and possibly sterols. The fractions were evaporated to dryness and stored at 0°C for GLC analysis.

FATTY ACID ISOLATION

The aqueous/methanol phase was acidified to pH 2 and extracted three times with 50 ml petroleum ether. The combined extracts were dried over anhydrous sodium sulfate and evaporated to dryness. The fatty acids were transferred in a total of 10 ml of benzene:methanol (1:1) to a 50 ml screw cap tube having a Teflon liner. Five ml of BF_3 - methanol were added, and the contents of the tube were heated at 100°C for five minutes. The fatty acid methyl esters so produced were extracted by addition of 10 ml of petroleum ether and 5 ml of distilled water. The aqueous phase was extracted a second time with 5 ml of petroleum ether, and the extracts were combined and dried. The extract was purified by preparative TLC on Silica Gel G plates (0.25 mm) developed with petroleum ether:ethyl ether:acetic acid (90:10:1). The band containing fatty acid methyl esters was scraped off. Methyl esters were extracted from the silica gel with methylene chloride, concentrated by evaporation of solvent, and analyzed by GLC.

GAS-LIQUID CHROMATOGRAPHY

All GLC analyses were performed on either a Hewlett-Packard 5710 chromatograph equipped with a HP 3380 integrator or a Hewlett-Packard 5830A chromatograph. Both chromatographs were equipped with dual columns and flame ionization detectors, and all analyses were done dual differentially to minimize baseline drift. All columns were of 1/8 inch o.d. stainless steel.

PE hydrocarbon fractions were analyzed on a 4 m columns packed with three percent SP2100 (Supelco Inc., similar to OV-101 methyl silicone) on 100/120 mesh Supelcoport with a temperature program from 150 to 325° at 4°/min and on 2.5 m columns packed with 10 percent SP1000 (Supelco, Inc., similar to FFAP) on 80/100 mesh Supelcoport with a temperature program from 120 to 250° C at 8°/min. BZ hydrocarbon fractions were analyzed on 3 m columns packed with 10 percent SP2100 on 100/120 mesh Supelcoport, programming from 200 to 330° at 4°/min. Fatty acid methyl esters were analyzed on 2 m columns packed with 10 percent SP-216-PS (Supelco, Inc., similar to diethylene glycolsuccinate) on 100/120 mesh Supelcoport, programming from 150 to 190° C at 4°/min with a two-minute hold at 150° C. Carrier gas for all column types was nitrogen. Flow rates were adjusted to optimize column efficiencies.

Qualitative analysis of chromatograms from the PE and BZ hydrocarbon fractions were done by the retention index system Kovats (1965). Fatty acid methyl esters were tentatively identified by comparison of their retention times with those of authentic standards.

Quantitative analysis of the PE hydrocarbon fraction was accomplished by addition of a known quantity of n-tetradecane (n-C14) to each sample immediately prior to injection. This alkane was a negligible component in these samples. Daily calibration of the chromatographic system was performed by injection of a quantitative mixture of authentic standards. Response factors relative to n-C14 were calculated for the 19 alkanes in the mixture. Response factors for peaks other than these alkanes in the chromatograms were estimated by linear interpolation according to retention index.

A known quantity of n-hexadecane (n-C16) was added to each BZ hydrocarbon fraction prior to injection. Response factors relative to n-C16 were calculated for six authentic aromatic hydrocarbon standards and for squalene, and the mean value was used as an estimate for all other peaks in the chromatograms.

Fatty acid quantitation was achieved by adding a known quantity of n-heptadecanoic acid to the aqueous/methanol phase prior to acidification and extraction. Response factors based upon authentic quantitative mixtures of fatty acid methyl esters were used.

EXTRACTION EFFICIENCY, REAGENTS, AND BLANKS

The overall procedure for extraction and analysis was tested by adding quantitative mixtures containing from two to four authentic standards to samples of pre-extracted Lake Huron sediment. Standard compounds were selected to be the same as or similar to compounds expected to be found in each of the four geolipid fractions. The sediment samples were then subjected to the overall extraction and analysis scheme. Triplicate determinations were done.

Mean recovery of the hydrocarbon mixtures was 90 ± 6 percent in the petroleum ether fraction and was 96 ± 6 percent in the benzene fraction. The benzene-methanol fraction mixture mean recovery was 89 ± 0 percent. The mean recovery of the fatty acid mixture was 98 ± 6 percent.

All chemicals used in this study were American Chemical Society reagent grade. Solvents were distilled once before use in all-glass stills equipped with 35 cm Widmer columns. New saponification glassware was saponified once prior to use. All glassware and apparatus was washed successively with 1 percent HCl, methanol, and methylene chloride immediately prior to use. Periodic procedural blanks showed only negligible quantities of contaminants as determined by GLC.

SECTION 4

RESULTS

SURFICIAL SAMPLES

Samples of surficial sediments were obtained for hydrocarbon and fatty acid analysis from two transects across the Goderich Basin and one transect along the axis of Saginaw Bay.

Table 2 summarizes fatty acid and hydrocarbon data obtained from these surficial sediment samples. Levels of fatty acid in the Goderich Basin samples range from 13.2 to 126.8 micrograms total acids per gram dry sediment. Concentrations of total normal alkane hydrocarbons and of total unsaturated hydrocarbons are also presented. These range from 1.6 to 12.8 and 2.2 to 46.5 $\mu\text{gm/gm}$, respectively. As shown in Figure 3, saturated hydrocarbon distributions are characterized by a number of resolved peaks overlying an unresolved complex mixture (UCM) of hydrocarbons. In the Goderich Basin sediments, concentrations of these unresolved hydrocarbons are between 16.1 and 381.7 $\mu\text{gm/gm}$.

In Saginaw Bay sediments fatty acid concentrations have a narrow range, between 95.8 and 116.8 $\mu\text{gm/gm}$, which is due in part to the relatively uniform sediment grain size of the four samples. Concentrations of both saturated and unsaturated hydrocarbons are higher in the Saginaw Bay samples than in the Goderich Basin samples, even though the central basin samples have equivalent or higher levels of total organic carbon. Normal alkanes are present at levels of from 19.9 to 27.5 $\mu\text{gm/gm}$, while unsaturated hydrocarbons range from 73.0 to 176.0 $\mu\text{gm/gm}$. Unlike the fatty acids and resolved hydrocarbons which exhibit relatively uniform concentrations, UCM amounts in these sediments increase from 349.4 $\mu\text{gm/gm}$ near the mouth of inner Saginaw Bay to 2669.0 $\mu\text{gm/gm}$ near the head of the Bay.

In Table 3, the distances from nearest land for each of the sediment samples are listed and various ratios are calculated. Hydrocarbon and fatty acid concentrations are given relative to total organic carbon levels and to each other. Saturated hydrocarbon/TOC ratios appear to be related to distance

TABLE 2. FATTY ACIDS AND HYDROCARBONS IN SURFICIAL SEDIMENTS FROM LAKE HURON BASIN TRANSECTS

Basin and Sample	Water Depth	Texture	TOC %	n-Acids $\mu\text{gm/gm}$	n-Alkanes $\mu\text{gm/gm}$	Unsat. HC's $\mu\text{gm/gm}$	UCM $\mu\text{gm/gm}$
Goderich, south 43-nearshore slope	27	sandy-silt	0.34	20.6	2.1	3.7	28.6
42-basin center	48	silty-clay	2.47	94.6	11.9	46.5	100.5
41-mid-lake ridge slope	44	sandy-silt	0.55	13.2	1.6	2.2	16.1
<hr/>							
Goderich, central 54-nearshore slope	42	silt	1.18	44.6	10.4	3.7	381.7
55-basin center	86	silty-clay	3.86	126.8	12.8	35.2	93.3
56-mid-lake ridge slope	55	sandy-silt	0.82	18.1	1.7	3.5	24.0
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Saginaw Bay 42A-head of bay	8	clay-silt	n.d.*	114.9	25.7	73.0	2669.0
30A	9	clay-silt	2.30	95.8	22.6	89.4	608.2
17A	11	clay-silt	2.78	116.8	19.9	64.0	469.3
6A-mouth of bay	12	clay-silt	2.54	113.5	27.5	176.0	349.4

*not determined

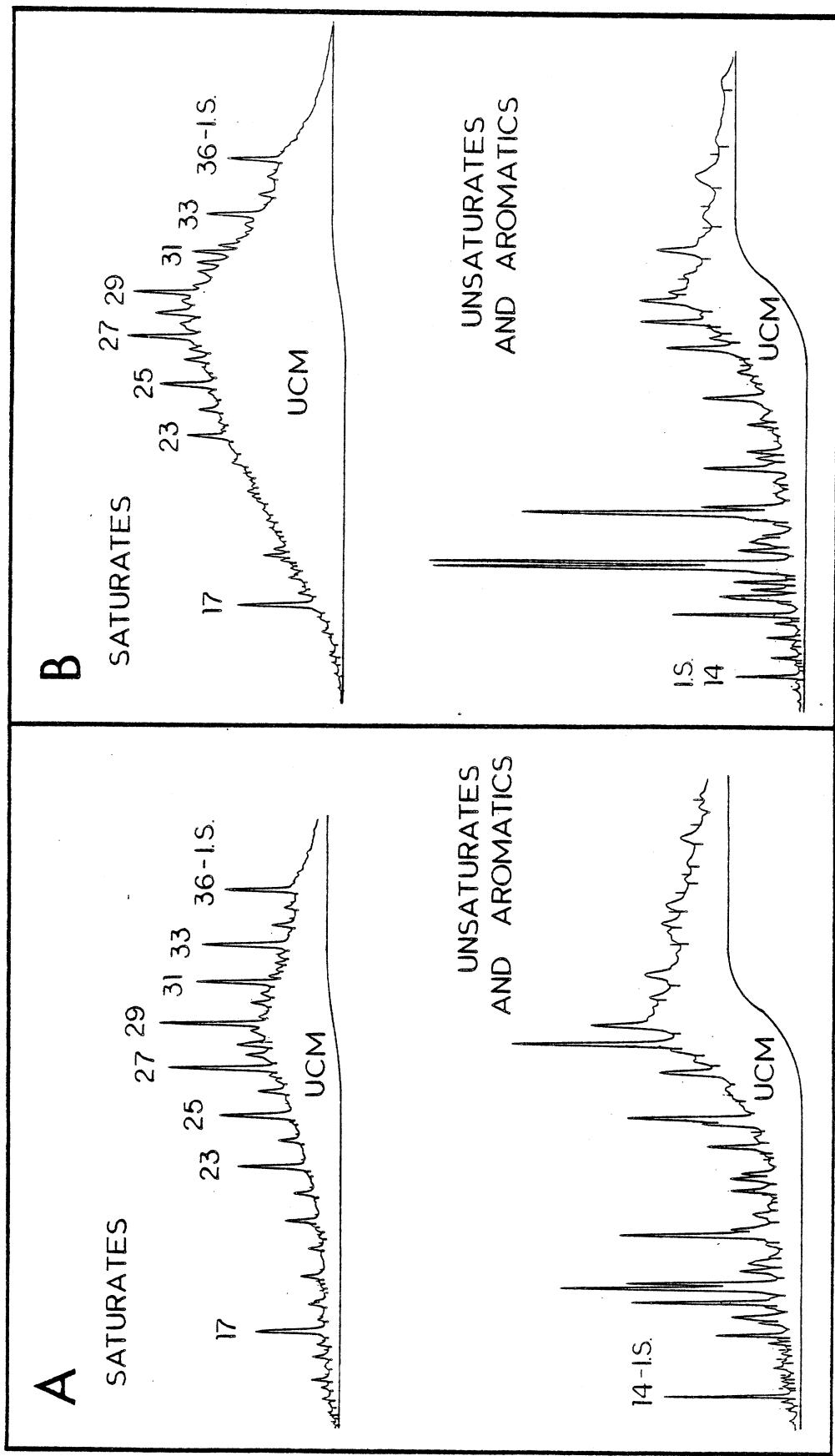


Figure 3. Gas chromatograms of hydrocarbons from surficial sediments in Lake Huron. Normal alkanes are labeled by carbon numbers. Boiling point ranges of saturated and unsaturated fractions are similar.
 A = Station 55 in Goderich Basin; B = Station 30A in Saginaw Bay.

TABLE 3. RATIOS OF ORGANIC MATTER COMPONENTS OF LAKE HURON SURFICIAL SEDIMENTS

Sample	Distance from Shore (km)	A	B	C	D	E	F
Goderich Basin	16	6.2	10.9	84.1	60.7	2.0	9.8
	15	8.8	3.1	323.5	37.8	2.1	4.3
	23	4.8	18.8	40.7	38.3	1.6	8.0
	28	3.3	9.1	24.2	32.8	2.2	9.9
	24	2.9	4.0	29.3	24.0	0.9	8.3
	35	2.1	4.2	29.3	22.1	1.6	10.7
Saginaw Bay	13	---	---	---	---	1.4	4.5
	17	9.8	38.9	264.4	41.7	1.5	4.2
	10	7.2	23.0	168.8	42.0	1.5	5.9
	6	10.8	69.3	137.6	44.8	1.4	4.1

A = total n-alkanes/total organic carbon ratio ($\times 10^4$)B = total polyunsaturated plus aromatic hydrocarbons/total organic carbon ratio ($\times 10^4$)C = unresolved complex mixture of aliphatic hydrocarbons/total organic carbon ratio ($\times 10^4$)D = total fatty acids/total organic carbon ratio ($\times 10^4$)

E = palmitoleic acid concentration/palmitic acid concentration

F = total acids/total n-alkanes

from land in the Goderich Basin samples. This may be a result of sediment texture; that is, finer-sized sediments have greater total surface area and therefore can have more organic matter associated with them. Similarly, total fatty acid/TOC ratios decrease with distance to land in the Goderich Basin sediments. The dominant acid in most of these samples was palmitoleic acid (16:1). This is indicated by the ratio of this acid to palmitic acid (16:0) being greater than unity, which suggests a dominantly recent biological source of these fatty acids (Farrington and Quinn, 1971a). Geolipid ratios in Saginaw Bay samples were relatively uniform, although average concentrations were higher than in the open lake.

The ratio of total normal fatty acids to total n-alkanes is also presented in Table 3. These two classes of compounds are biochemically related, and therefore this ratio can be used to compare geolipid contents of different sediments. Most of the Goderich Basin samples have ratios from 8 to 10, but the Saginaw Bay samples have ratios half this size. This implies that hydrocarbons are more important contributors to the total geolipid content of Saginaw Bay sediments than of Goderich Basin sediments.

SOUTHERN LAKE HURON, CORE SLH 74-12

Most of the data obtained from analyses of sediment cores have been summarized in graphical, rather than tabular, form. This has been done in order to condense the large volume of data and to facilitate both comparison of different cores and observation of trends of various components within a single core.

Distributions of total organic carbon and of the water content of core SLH 74-12 are presented in Figure 4. The relatively high level of organic carbon, three percent of total dry weight of sediment, is a reflection of the relatively fine grain-size of this sediment, a clay-silt. The general lack of change with depth of organic carbon concentration combined with a slight but regular decrease in water content due to compaction agrees with visual indications that this is a non-stratified sediment having no discontinuities.

The levels of total resolved hydrocarbons found at the 21 depths examined in this core are usually from 5 to 30 micrograms per gram dry sediment. At 1 to 2 cm it reaches 112 $\mu\text{gm/gm}$, and at 5 to 6 cm it is 122 $\mu\text{gm/gm}$. The total aromatic and unsaturated hydrocarbon contribution to the total hydrocarbons is shown in Figure 5. The greatest concentration of aromatic and unsaturated hydrocarbons occurs at 5 to 6 cm, and a similarly high level is found at 1 to 2 cm. Figure 5 also shows total aliphatic hydrocarbon concentrations. This profile shows the highest level of aliphatic hydrocarbons to be at 7 to 8 cm and a second peak at 4 to 5 cm.

The contribution of n-alkanes to total aliphatic hydrocarbons is presented in Figure 6. Data was obtained from SP-1000 columns because of their superior separation and resolution of n-alkanes from branched and monounsaturated alkanes. The percentage of n-alkanes is about 60 percent throughout most of this core. Carbon Preference Indices (CPI) profiles are presented for the n-alkane concentrations as calculated by the procedure of Cooper and Bray (1963). CPI values from the polar column data range from 1.2 to 3.3 with an average near 2.1.

The vertical profile of total fatty acids is shown in Figure 7. Concentrations drop from 138 $\mu\text{gm/gm}$ dry sediment at the surface to around 40

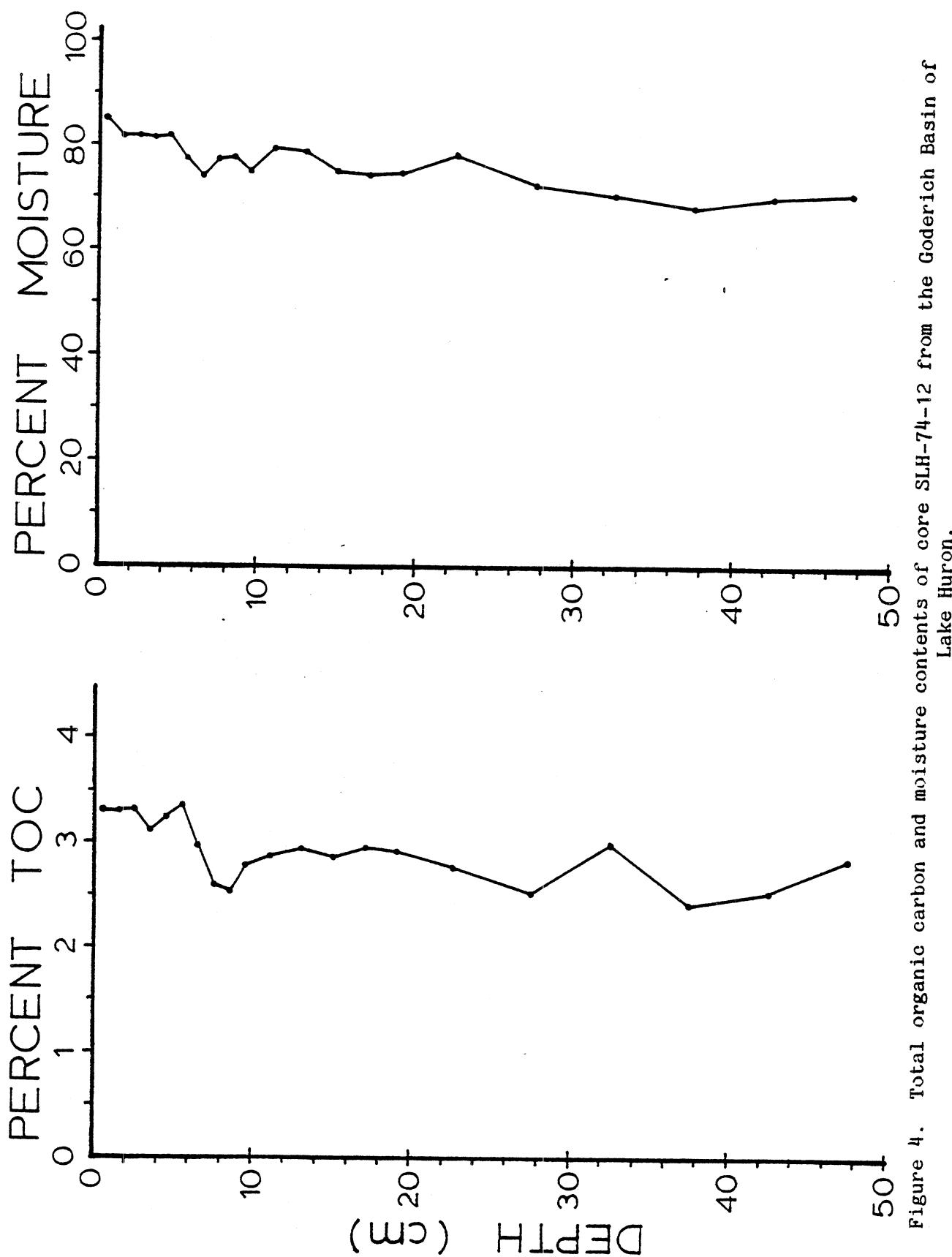


Figure 4. Total organic carbon and moisture contents of core SLH-74-12 from the Goderich Basin of Lake Huron.

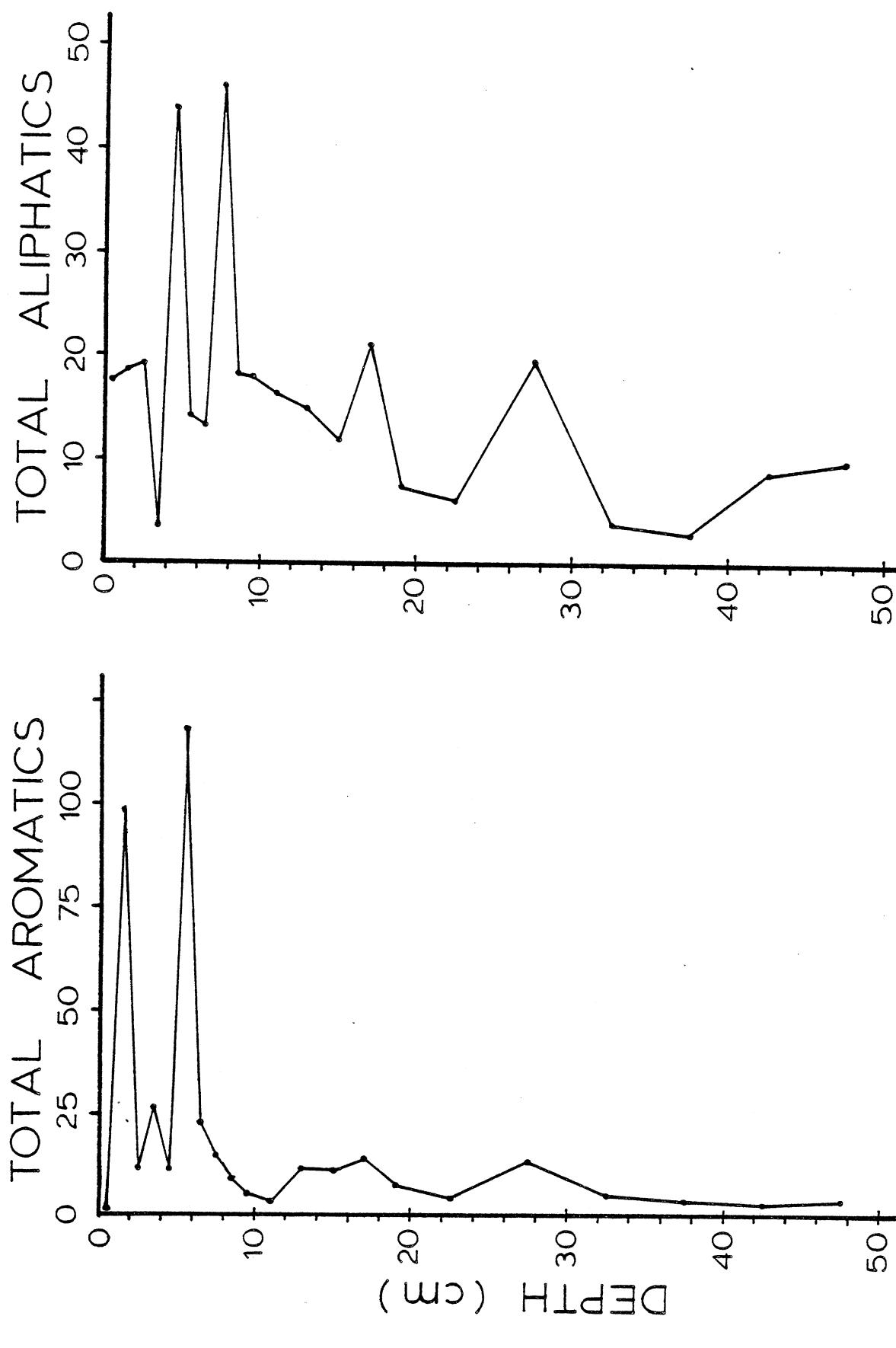


Figure 5. Total aromatic and unsaturated hydrocarbon content and total aliphatic hydrocarbon content in core SLH-74-12 from the Goderich Basin of Lake Huron. Concentrations are given in micrograms per gram dry sediment and are derived from 3% SP2100 GC columns.

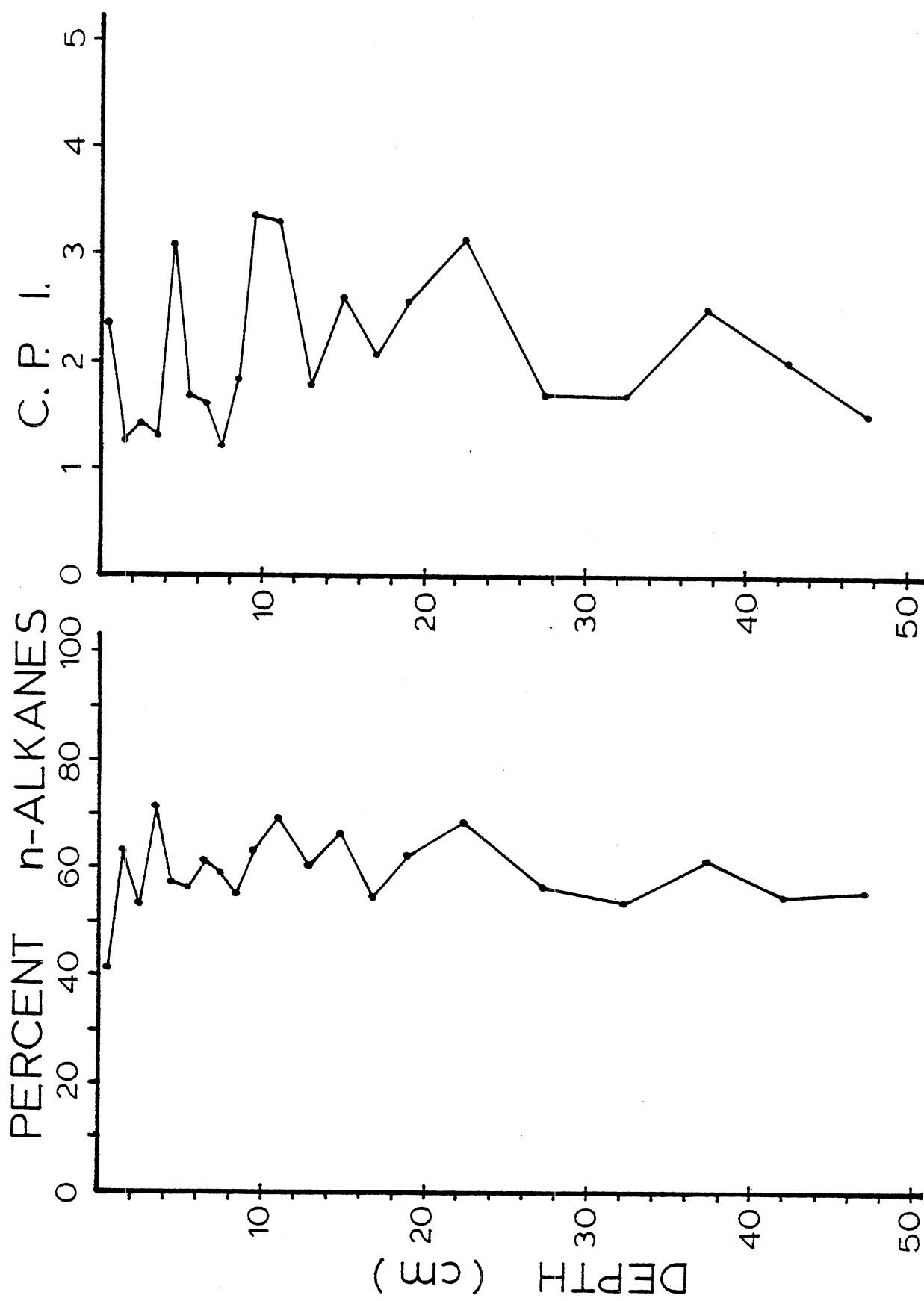


Figure 6. Normal alkane contributions to total aliphatic hydrocarbons and carbon preference indices (Cooper and Bray, 1963) for core SLH-74-12. Data are derived from 10% SP1000 columns.

CORE SLH74-12

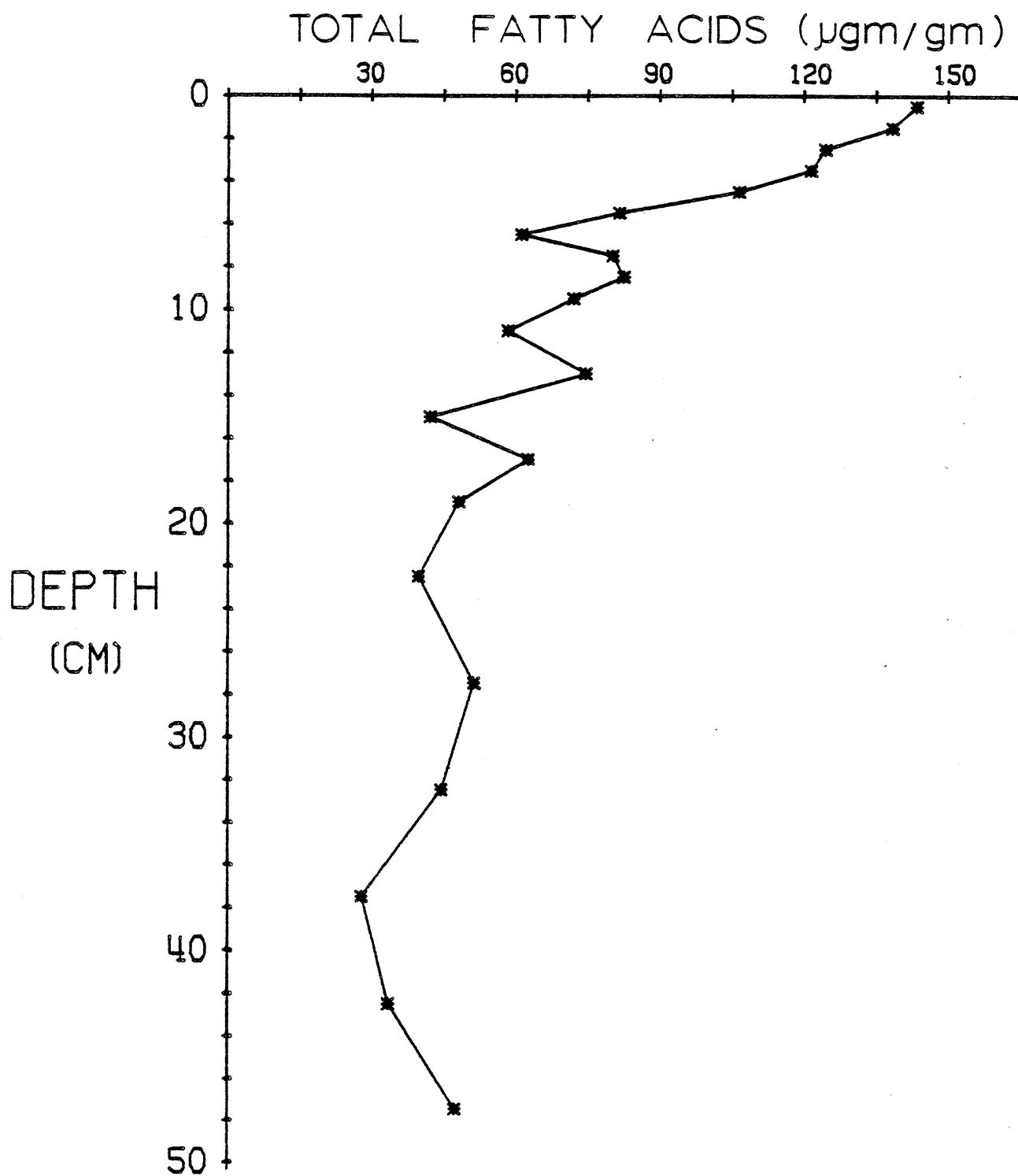


Figure 7. Total fatty acid content in core SLH-74-12. Concentrations are derived from SP-216-PS columns and given in micrograms per gram dry sediment.

$\mu\text{gm/gm}$ dry sediment at 20 cm depth and then change little to 50 cm. This is unlike the hydrocarbon concentrations in Figure 5 which with the exception of two peaks change little with depth. Much of the decrease in fatty acid concentration from 9 to 20 cm is due to loss of unsaturated acids. This is shown in Figure 8 in the large decrease in the ratio of unsaturated to saturated acids from depths of 3 to 14 cm in the sediment. The loss of unsaturated components of total fatty acids is further illustrated in Figure 9, showing histogram distributions of fatty acids at 1 to 2 cm and 10 to 12 cm. Unsaturated palmitoleic and oleic acids, represented by dashed lines, dominate the 1 to 2 cm fatty acid composition. At 10 to 12 cm, the saturated acids palmitic, myristic, and stearic, represented by solid lines, dominate the composition.

SOUTHERN LAKE HURON, CORE SLH 75-58

The amount of total organic carbon found in eighteen sections of this core is shown graphically in Figure 10, and the percent moisture in nine sections is also shown in this figure. Levels of both parameters are highest at the surface and lowest at a depth of 3 to 5 cm in the sediment. This depth corresponds to a coarse-grained sandy layer. Below 9 to 10 cm, organic carbon is about one percent of the total sediment weight, and the moisture content is around 50 percent at the bottom of the core. This bottom 40 cm was comprised of clay-size sediment.

Figure 11 shows the distribution of total benzene fraction hydrocarbons (unsaturates and aromatics). A level of 26 $\mu\text{gm/gm}$ is found at the surface, but only 1 to 2 $\mu\text{gm/gm}$ below 6 cm. Total aliphatic hydrocarbons follow the pattern of total aromatic hydrocarbons, as also shown in Figure 11. Below the surface layer, only 1 to 3 micrograms total aliphatic hydrocarbons are found in each gram of sediment.

The percent contribution of n-alkanes to total aliphatic hydrocarbons is shown in Figure 12. The percentage of n-alkanes shows little variation with depth and remains between 45 percent and 60 percent. This figure also presents CPI values of n-alkanes. These values average 1.5 and range from 1.3 to 1.8.

SAGINAW BAY, CORE SB 75-30A

As shown in Figure 13, the concentration of total organic carbon decreases from about 2.4 percent in surficial sediment to about 1.4 percent at the bottom of this 60-cm core. The smooth decrease in water content, also presented in this figure, suggests water loss due to compaction with depth and the absence of stratigraphic variations in this core. Visual inspection of the core at the time of sampling indicated no grain-size changes with depth. Hence this core is similar to core SLH 74-12 in having no discontinuities but is dissimilar in its total organic carbon profile.

Concentrations of total resolved aliphatic hydrocarbons are plotted versus depth in Figure 14. These concentrations are generally between 10 and 50 μgm per gram of dry sediment, but higher levels of 310 $\mu\text{gm/gm}$ and 120 $\mu\text{gm/gm}$ exist at depths of 12 to 14 cm and 30 to 35 cm, respectively.

The contributions of n-alkanes to the total aliphatic hydrocarbon content of the various sections of this core of Saginaw Bay sediment are given in

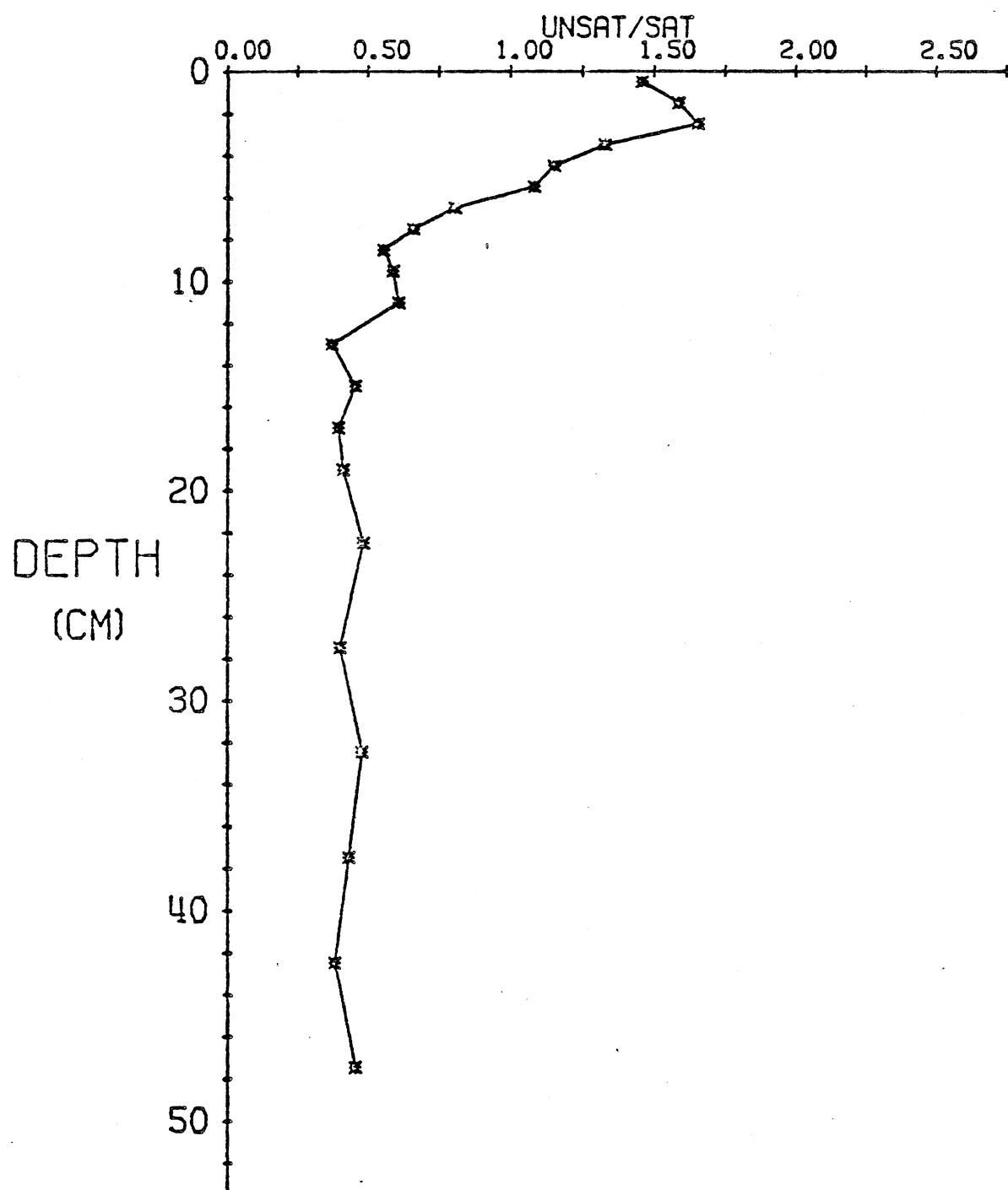


Figure 8. Ratios of total unsaturated fatty acid content to total saturated fatty acid content in core SLH-74-12.

n-FATTY ACIDS, CORE SLH 74-12

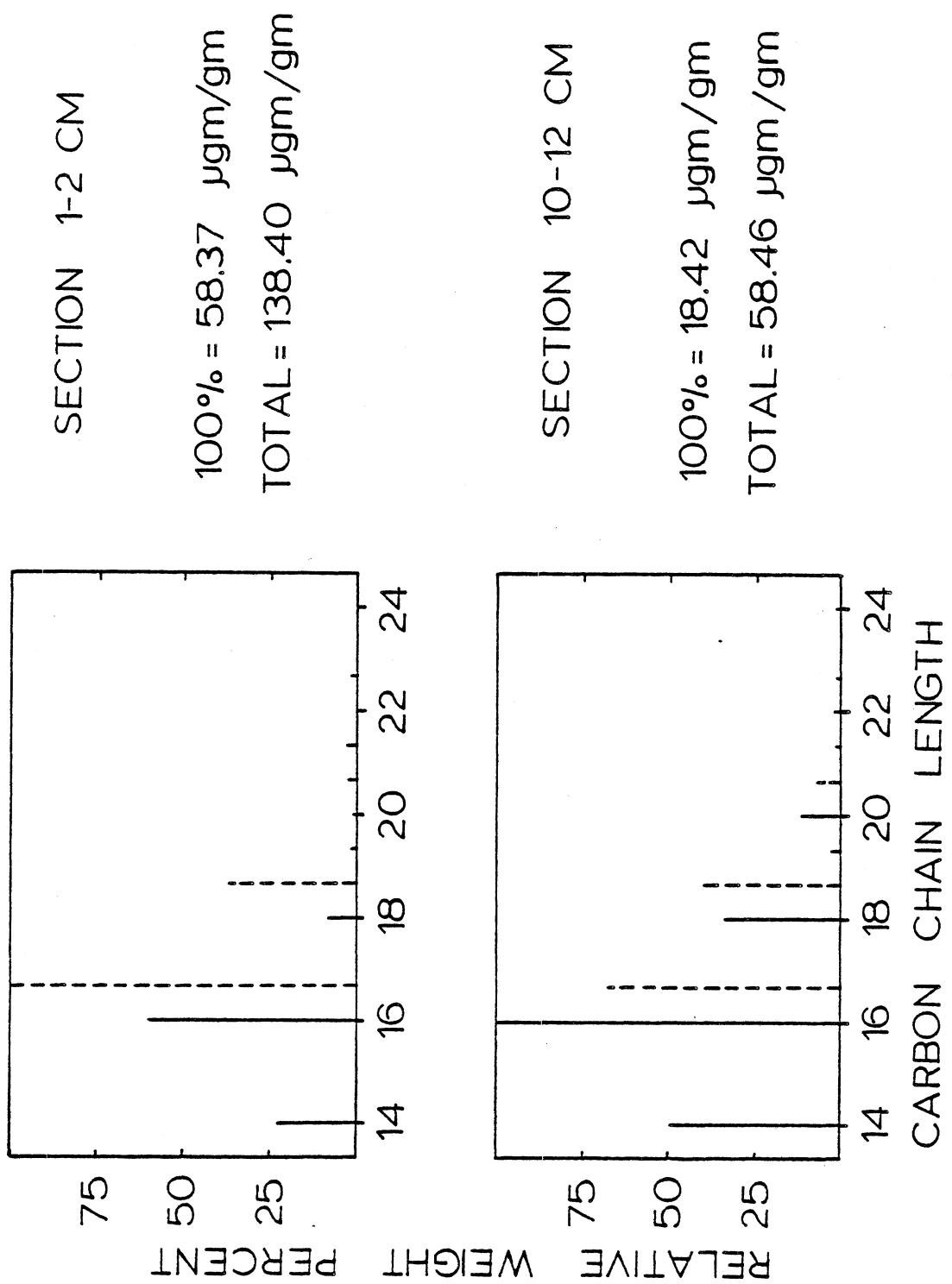


Figure 9. Histograms of n-fatty acid distributions at two depths in core SLH-74-12 from the Goderich Basin of southern Lake Huron. Distributions normalized to major fatty acid.

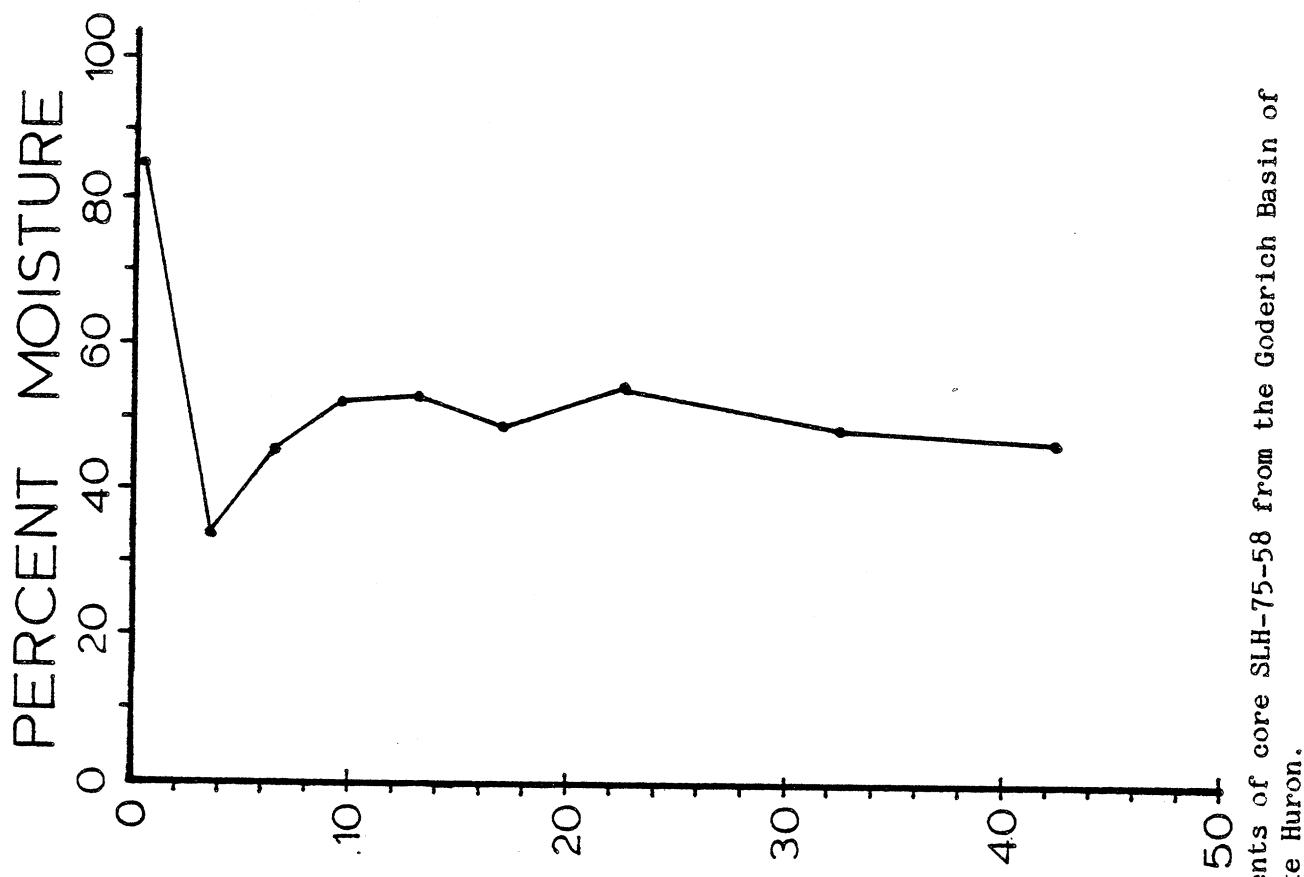
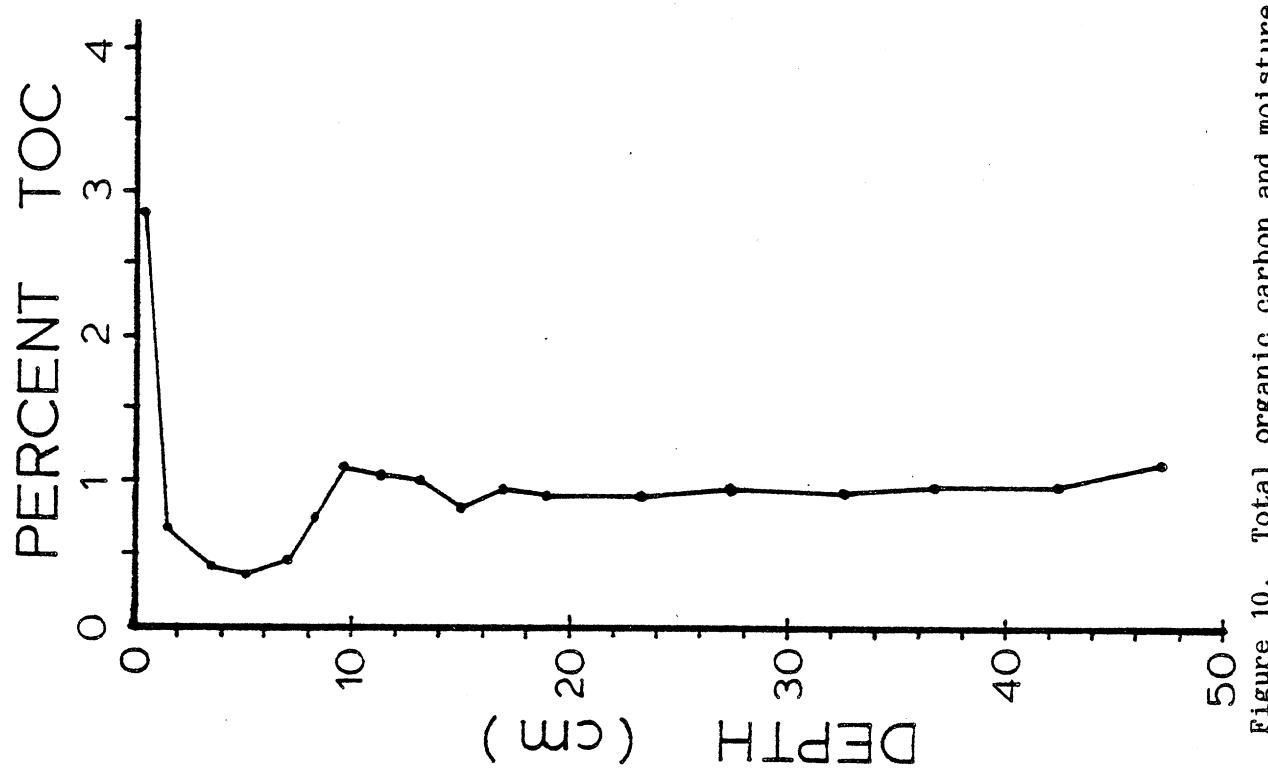


Figure 10. Total organic carbon and moisture contents of core SLH-75-58 from the Goderich Basin of Lake Huron.

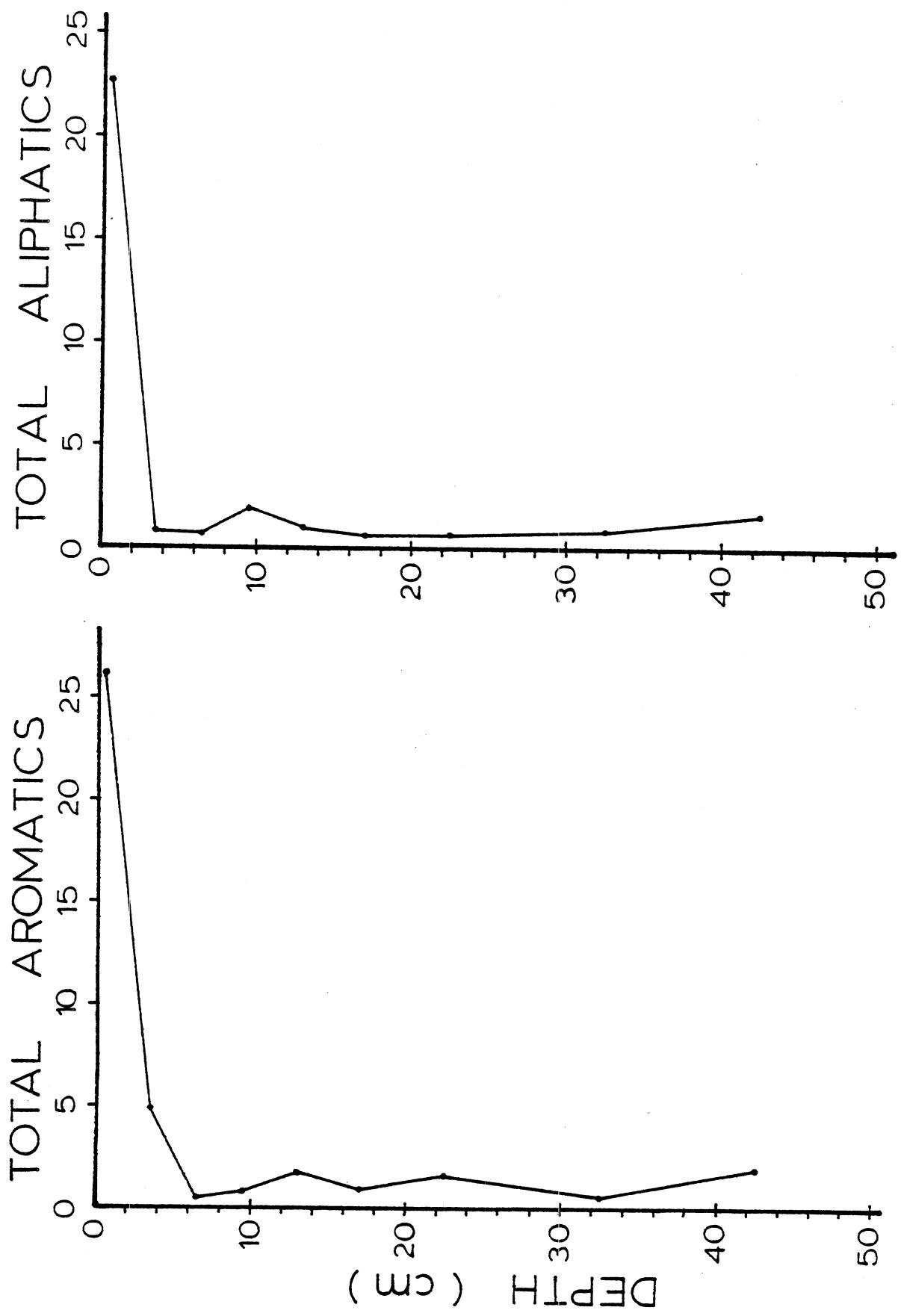


Figure 11. Total aromatic and unsaturated hydrocarbon content and total aliphatic hydrocarbon content in core SLH-75-58 from the Goderich Basin of Lake Huron. Concentrations are given in micrograms per gram dry sediment and are derived from 3% SP2100 columns.

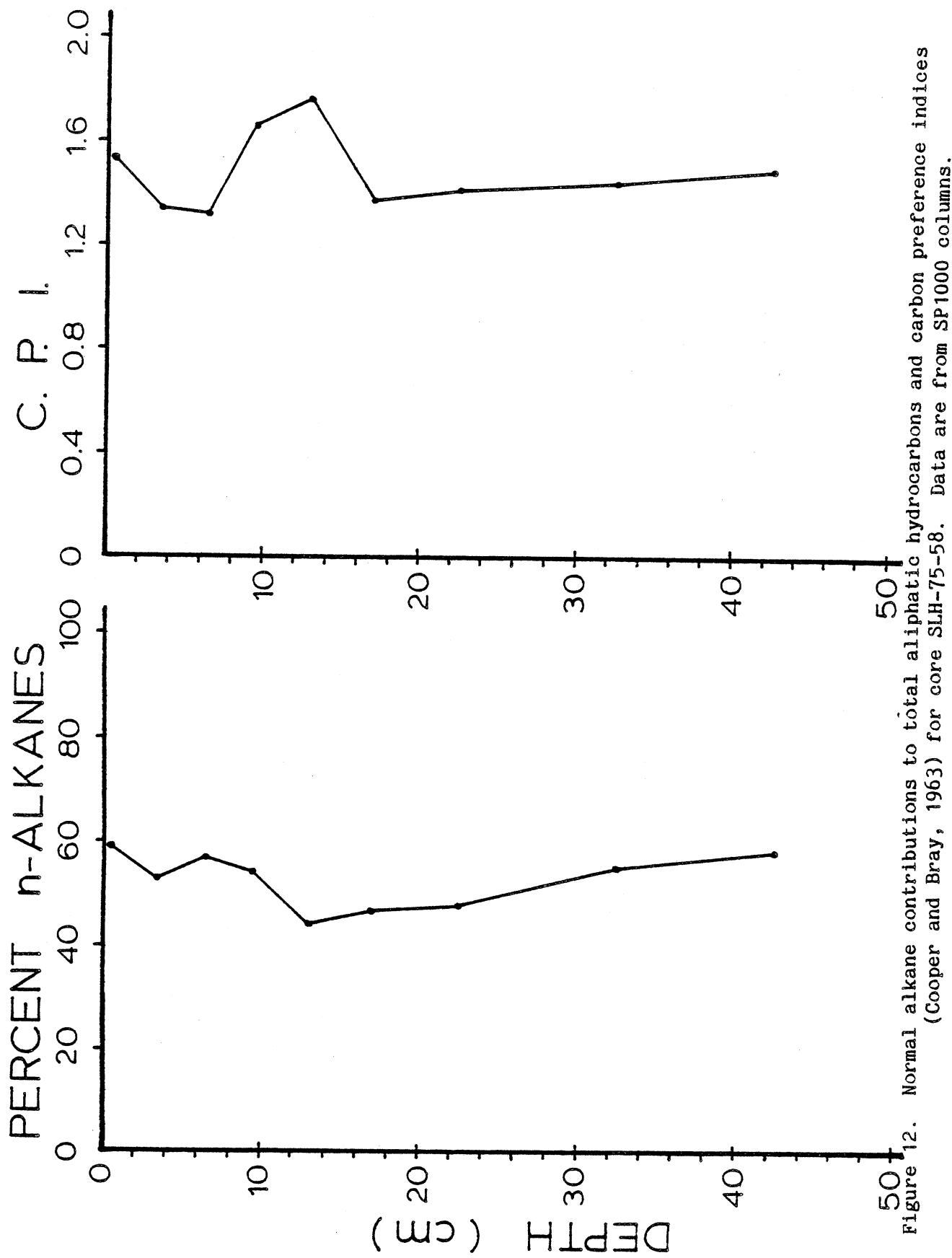


Figure 12. Normal alkane contributions to total aliphatic hydrocarbons and carbon preference indices (Cooper and Bray, 1963) for core SLH-75-58. Data are from SP1000 columns.

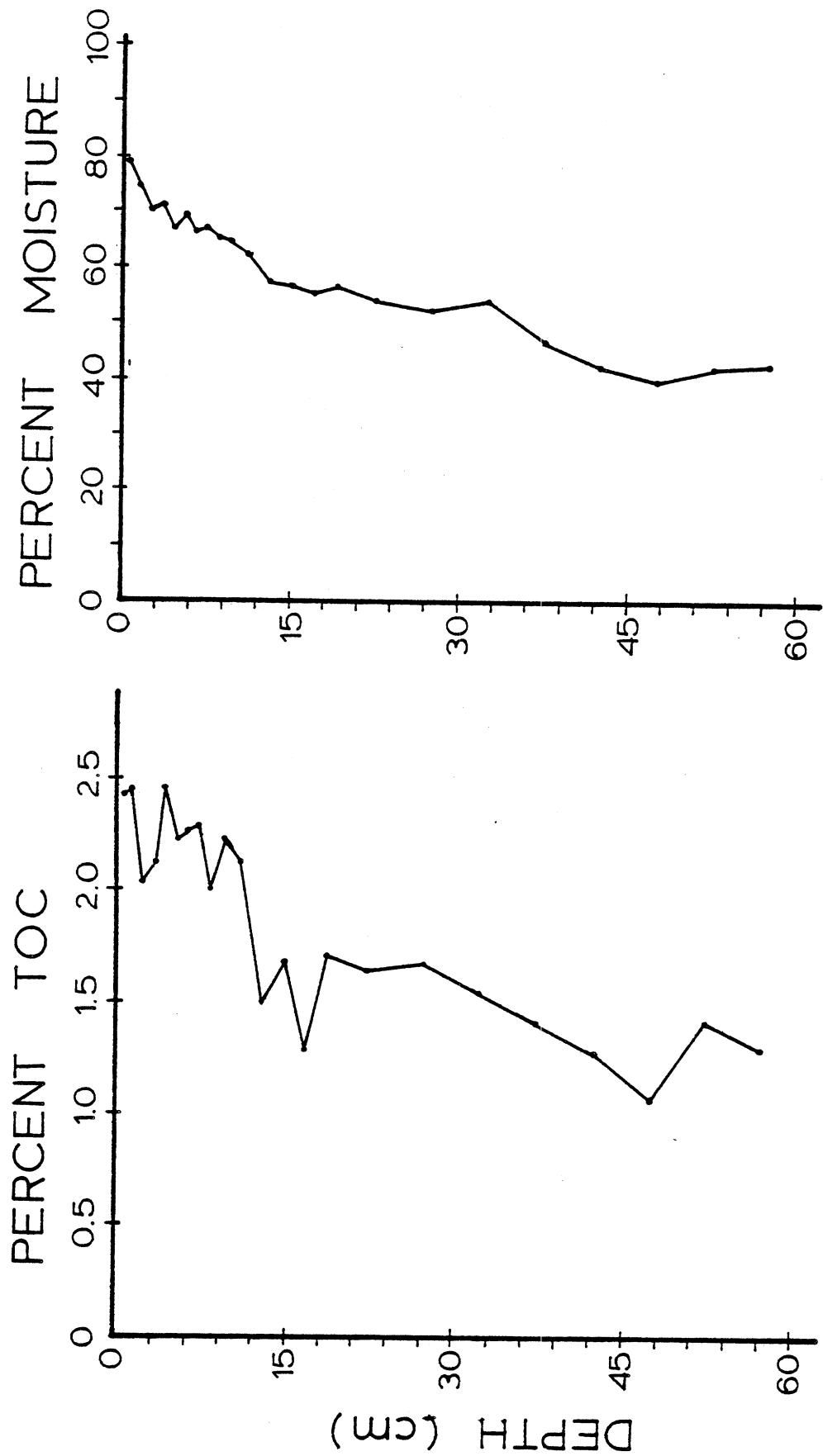


Figure 13. Total organic carbon and moisture contents of core SB-75-30A from Saginaw Bay.

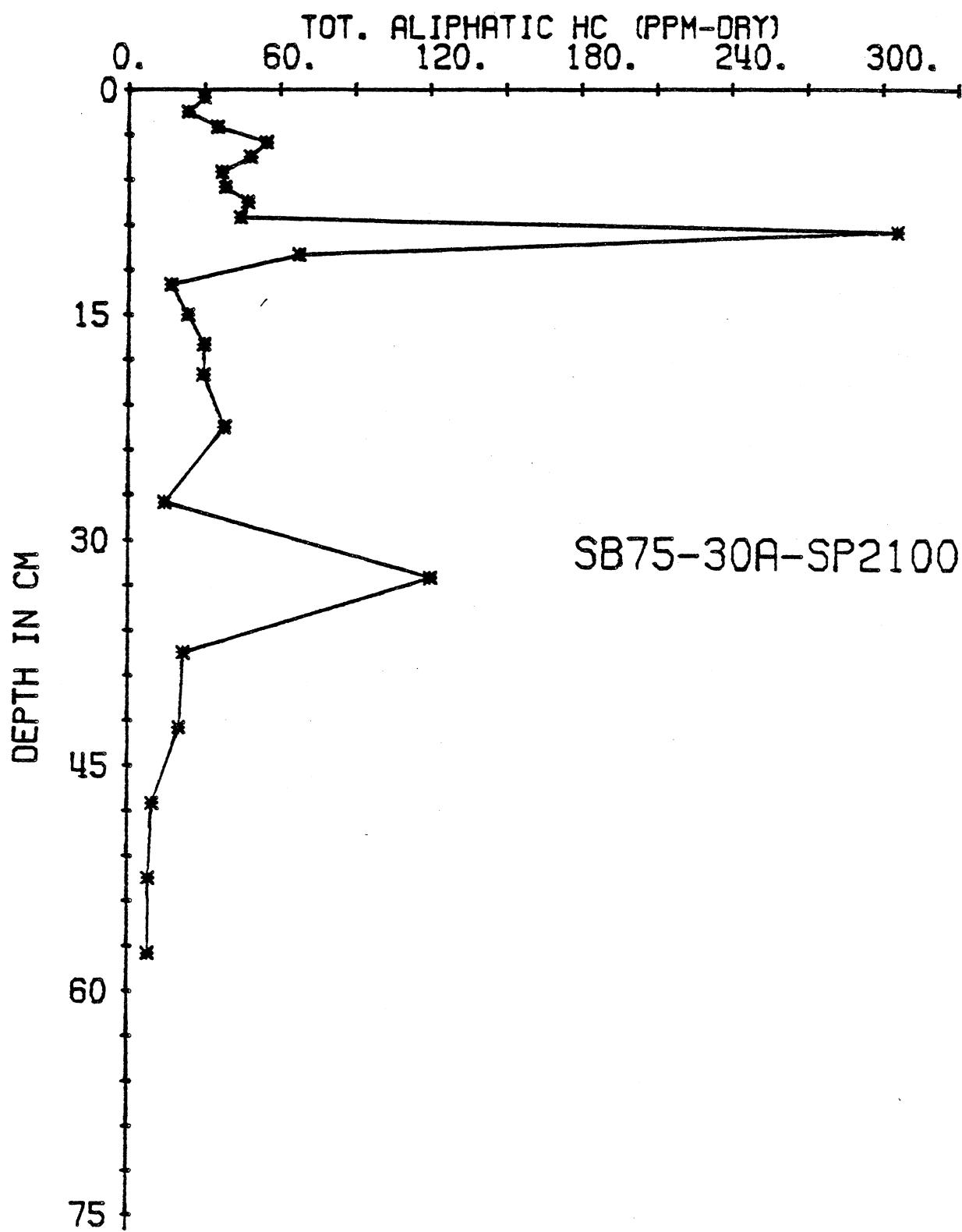


Figure 14. Total aliphatic hydrocarbon content in core SB-75-30A from Saginaw Bay. Concentrations are given in micrograms per gram dry sediment and are derived from 3% SP2100 columns.

Figure 15. These range between 38 and 93 percent. The contribution of n-alkanes appears to be different above a depth of 35 cm than below this point. The average value from the sediment surface to 35 cm is 52 percent, while from 35 cm to the core bottom it is 81 percent. The CPI values of these n-alkanes are also shown in Figure 15. They range from 0.8 to 6.8 and average 3.2. Both the lowest and the highest values of this comparative index are found in the top 12 cm of this core.

Fatty acid concentrations are shown in Figure 16 as separate plots for total acids of carbon chain lengths of 20 carbon atoms and less and for acids having chain lengths greater than 20 carbon atoms. The longer-chain acids contribute between 2 and 8 μgm total acids per gram dry sediment and have little change related to sediment depth. Surficial sediment concentration is 102 $\mu\text{gm/gm}$ while the concentration below 35 cm is about 10 $\mu\text{gm/gm}$. As indicated by the ratio of the concentrations of the unsaturated 18-carbon acid to that of its saturated analog in Figure 17, the levels of fatty acids having double bonds in their carbon chains decrease more quickly than do those of saturated acids.

In addition to the major, depth-related change in fatty acids observed in this core, there was an important change in the size of the unresolved complex mixture of hydrocarbons underlying the resolved peaks in the chromatograms of aliphatic hydrocarbons from this core. Figure 18 compares the chromatogram of surface hydrocarbons with that of hydrocarbons found at a depth of 50 to 55 cm. The concentration of total hydrocarbons, determined by planimetry, decreases from 1115 $\mu\text{gm/gm}$ to 6.7 $\mu\text{gm/gm}$ from the surface to the deep sample. The unresolved complex mixture changes from 1000 $\mu\text{gm/gm}$ at the surface to 4.0 $\mu\text{gm/gm}$ near the core bottom. This decrease is not linear; most of it occurs at a depth of 25 to 30 cm in the core. This depth corresponds to a sediment age of 100 to 120 years.

Combined gas chromatography-mass spectrometry was performed on hydrocarbon extracts from two sections of core SB75-30A. Dr. R. A. Brown of Exxon Research and Engineering Company, Linden, N. J., graciously offered the use of his laboratory for these analyses. The saturated hydrocarbon fraction at 1 to 2 cm consisted of 14 percent paraffins and 86 percent cycloparaffins; at 50 to 55 cm it was 40 percent paraffins and 60 percent cycloparaffins. The unsaturated fractions from both sections consisted almost entirely of nonbiogenic polycyclic aromatic hydrocarbons.

Dr. William M. Sackett of Texas A & M University kindly performed carbon isotope measurements on three sections of this Saginaw Bay sediment core. The ^{13}C values relative to the PDB standard were -26.7 per mille for the 4 to 5 cm section, -26.7 per mille for the 25 to 30 cm section, and -26.8 per mille for the 45 to 50 cm section.

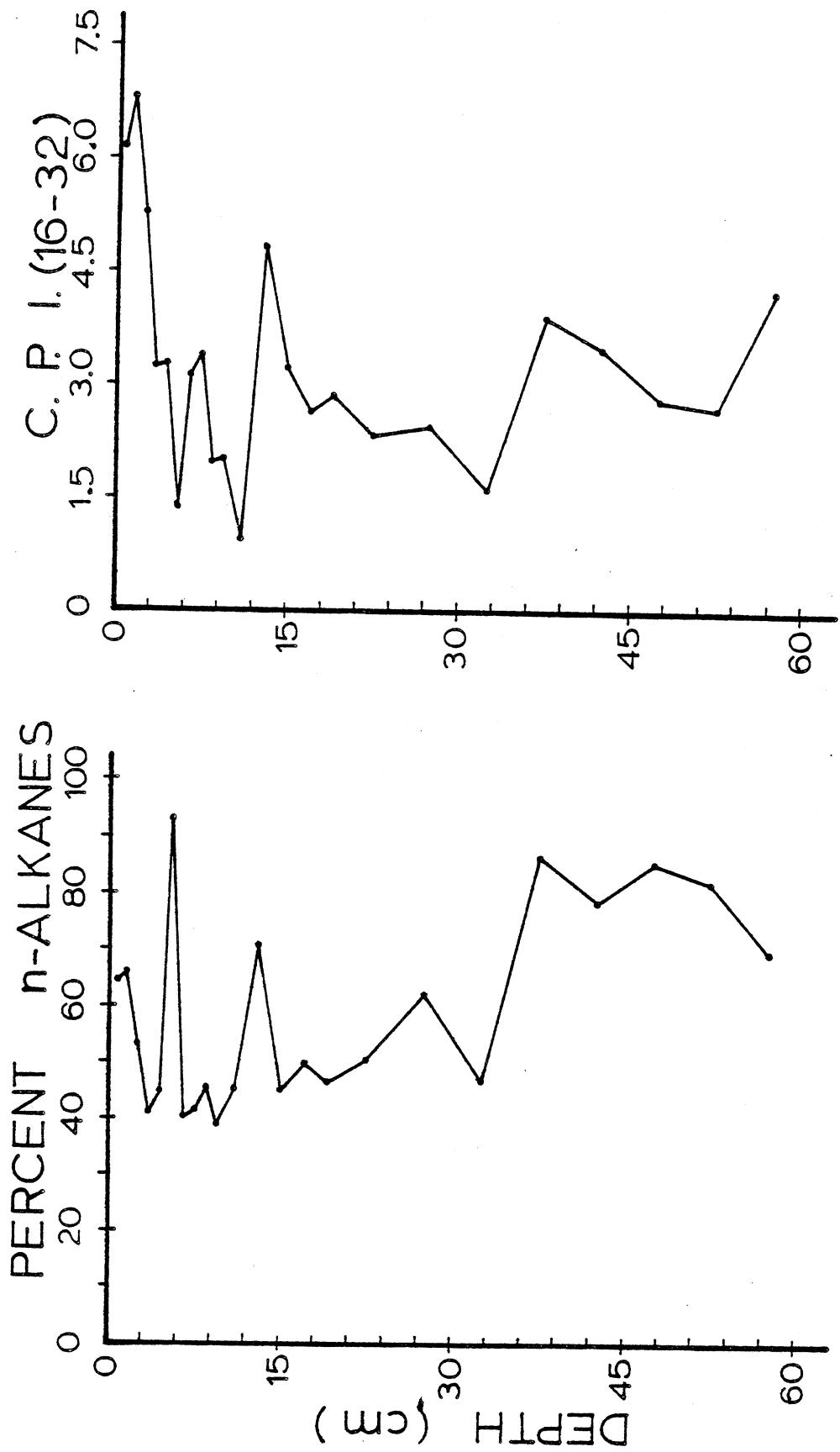


Figure 15. Normal alkane contributions to total aliphatic hydrocarbons and carbon preference indices (Cooper and Bray, 1963) for core SB-75-30A from Saginaw Bay. Data are from SP1000 columns.

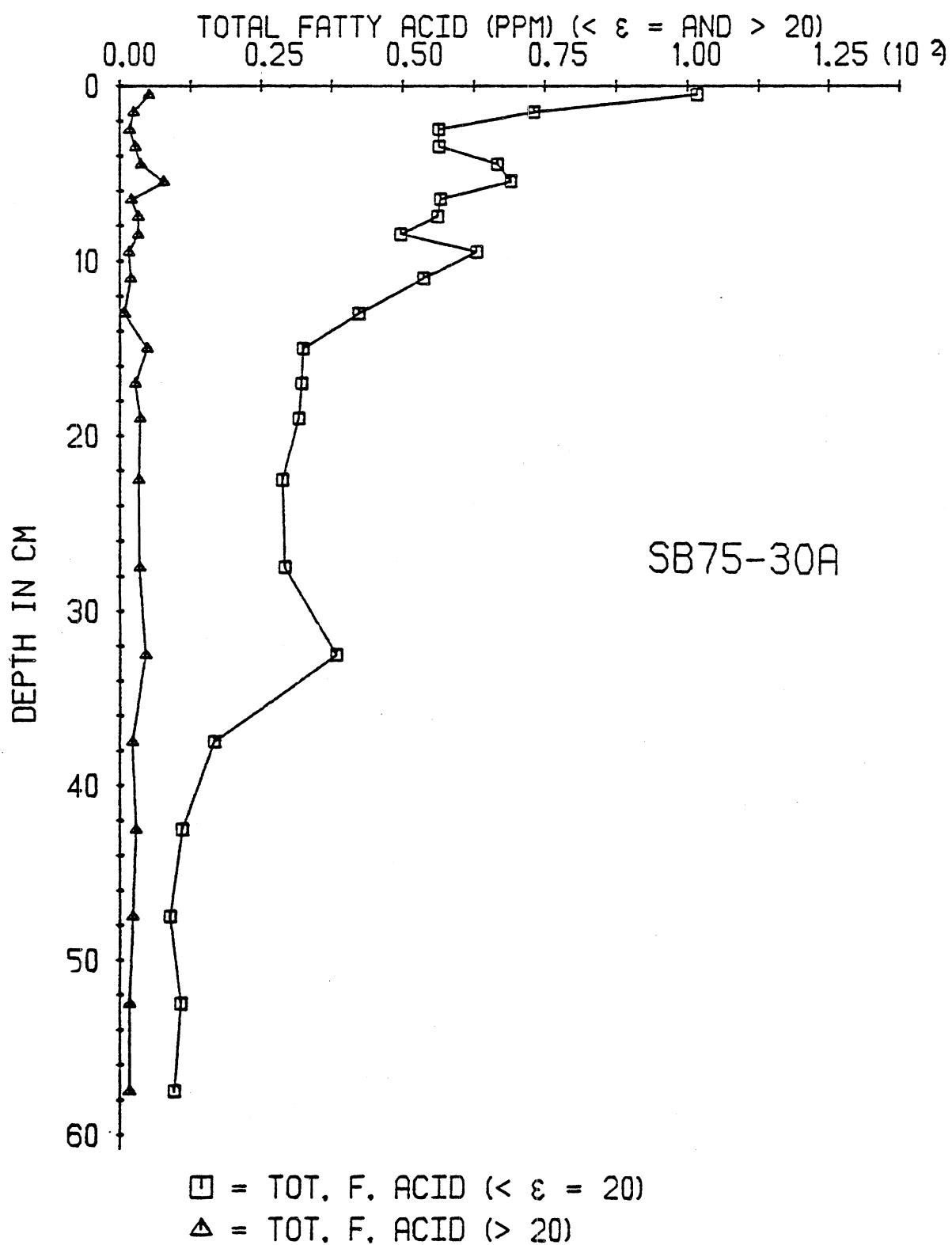


Figure 16. Total fatty acid content of core SB-75-30A from Saginaw Bay. Concentrations given in micrograms per gram dry sediment for both total acids up to chain length of C20 and total acids longer than C20. Data are derived from SP-216-PS columns.

SB75-30A-SP2100

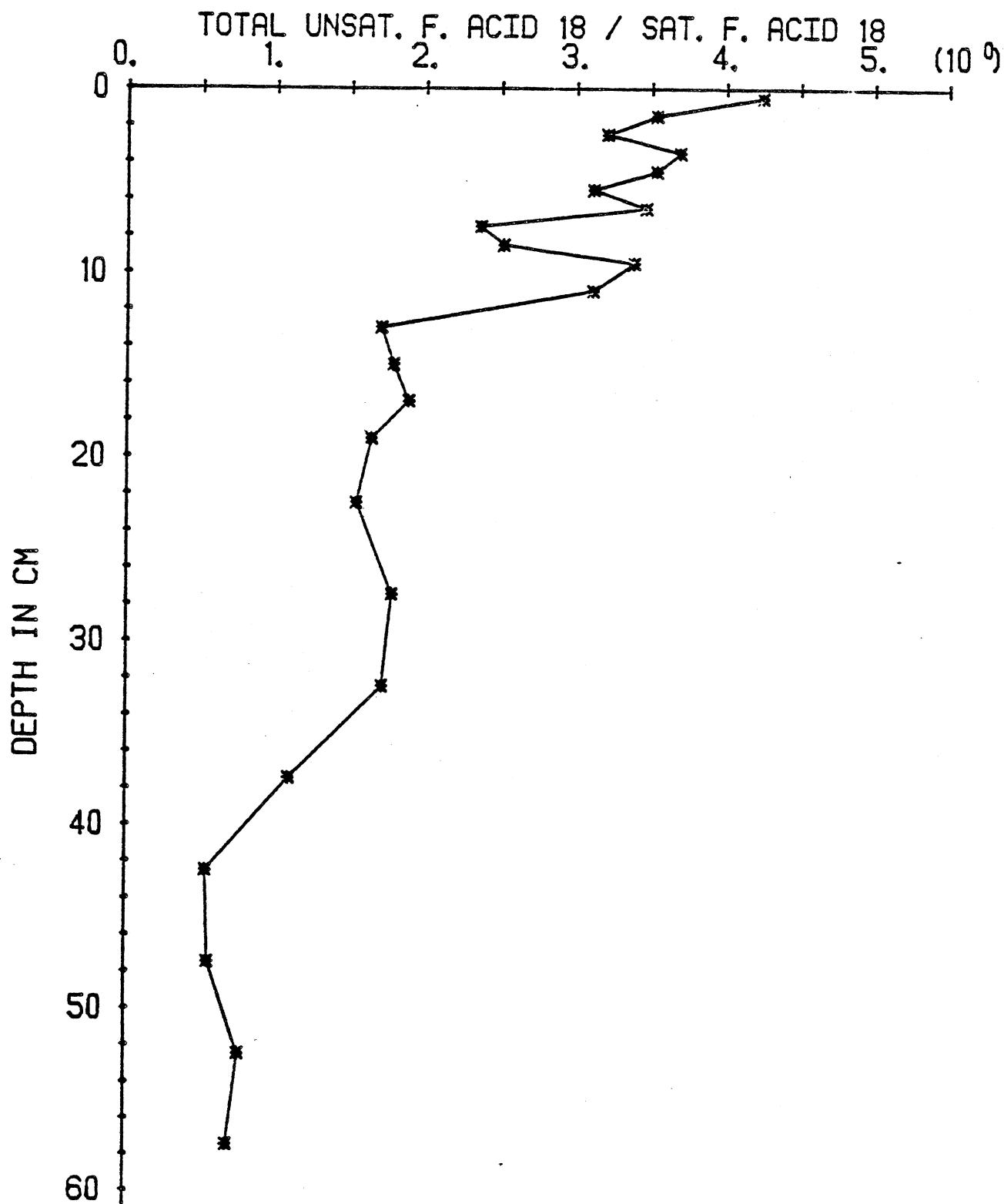


Figure 17. Ratios of oleic (18:1) to stearic (18:0) fatty acid concentrations in core SB-75-30A.

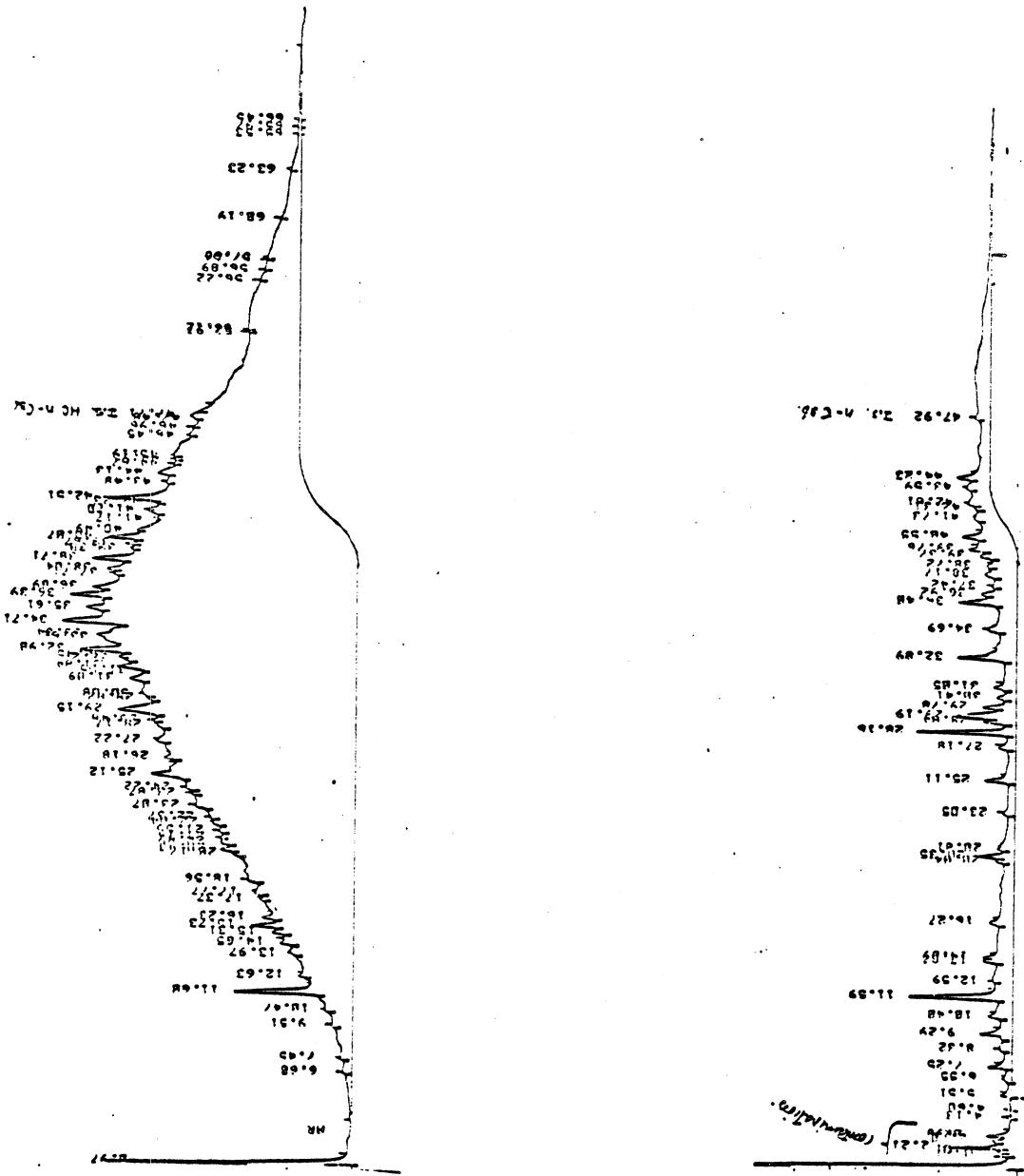


Figure 18. Gas chromatograms of aliphatic hydrocarbons from depths of 0-1 cm and 50-55 cm in core 75-30A from Saginaw Bay of Lake Huron. Chromatogram baselines indicated by solid lines. GC conditions: 4 m x 2.1 mm ID 3% SP2100 on Supelcopor 80-100 column, operated dual differentially from 150-324°C at 4°C/min. Internal standard indicated by I.S.

SECTION 5

DISCUSSION

SURFICIAL SEDIMENTS

The total organic carbon values reported in Table 1 are within the range of values reported by Kemp (1971) for Lake Huron surficial sediments. Therefore, these sediment samples appear not to be atypical, and may indeed be representative, of the Lake Huron basin sediments from which they were collected.

While actual grain size measurements are not available, the visual textural descriptions of these samples suggests a rough correlation between smaller grain size and higher organic carbon levels. Kemp (1971) found a good correlation between the amounts of clay-size sediment particles and of organic carbon in sediments from Lakes Erie and Ontario and further states that this is likely to be true in Lake Huron sediments as well. Because the clay-size fraction of sediment contains a large proportion of clay materials, it may well be that the levels of organic carbon shown in Table 1 reflect in part variations in clay mineral content of these samples rather than simple grain size differences. Such mineralogical variations would affect organic carbon levels due to the large sorptive surface areas possessed by clay minerals.

In Goderich Basin, the concentrations of n-alkanes and fatty acids are highest in the silty-clay sediments of the deep center stations. However, as shown in Table 3 the total n-alkane/TOC and total fatty acids/TOC ratios decrease progressively from the nearshore slope locations to the mid-lake ridge locations. Accompanying this is a general decrease in the 16:1/16:0 fatty acid ratio which may indicate a change in the source of these materials. Such changes in the contribution of these geolipid constituents to the total organic load of sediments with distance from shore imply a terrigenous origin for much of the n-alkanes and fatty acids, perhaps combined with alteration of these materials. In contrast, the ratio of total unsaturated hydrocarbons/TOC shows no similar trend and is instead highest in the basin-center stations within each transect (42 and 55) where organic carbon concentrations are highest. This suggests that most of these unsaturated hydrocarbons may not be directly derived from land sources and may be related to the amount of organic matter in the sediment, to sediment texture or mineralogy, or to populations of aquatic organisms. As an example of the latter possibility, high levels of unsaturated hydrocarbons have been found in marine benthic organisms (Youngblood *et al.*, 1971; Youngblood and Blumer, 1973; Meyers, 1977). It should be pointed out, however, that Thomas *et al.* (1973) could find no correlation between benthos concentration and organic carbon levels in the surficial sediments of Lake Huron, and thus the source of unsaturated hydrocarbons is not obvious in these samples.

Figure 19 gives comparisons of fatty acid distributions in Goderich Basin surficial sediments which provide indications of several possible geolipid sources. All show a strongly biogenic pattern characterized by large amounts

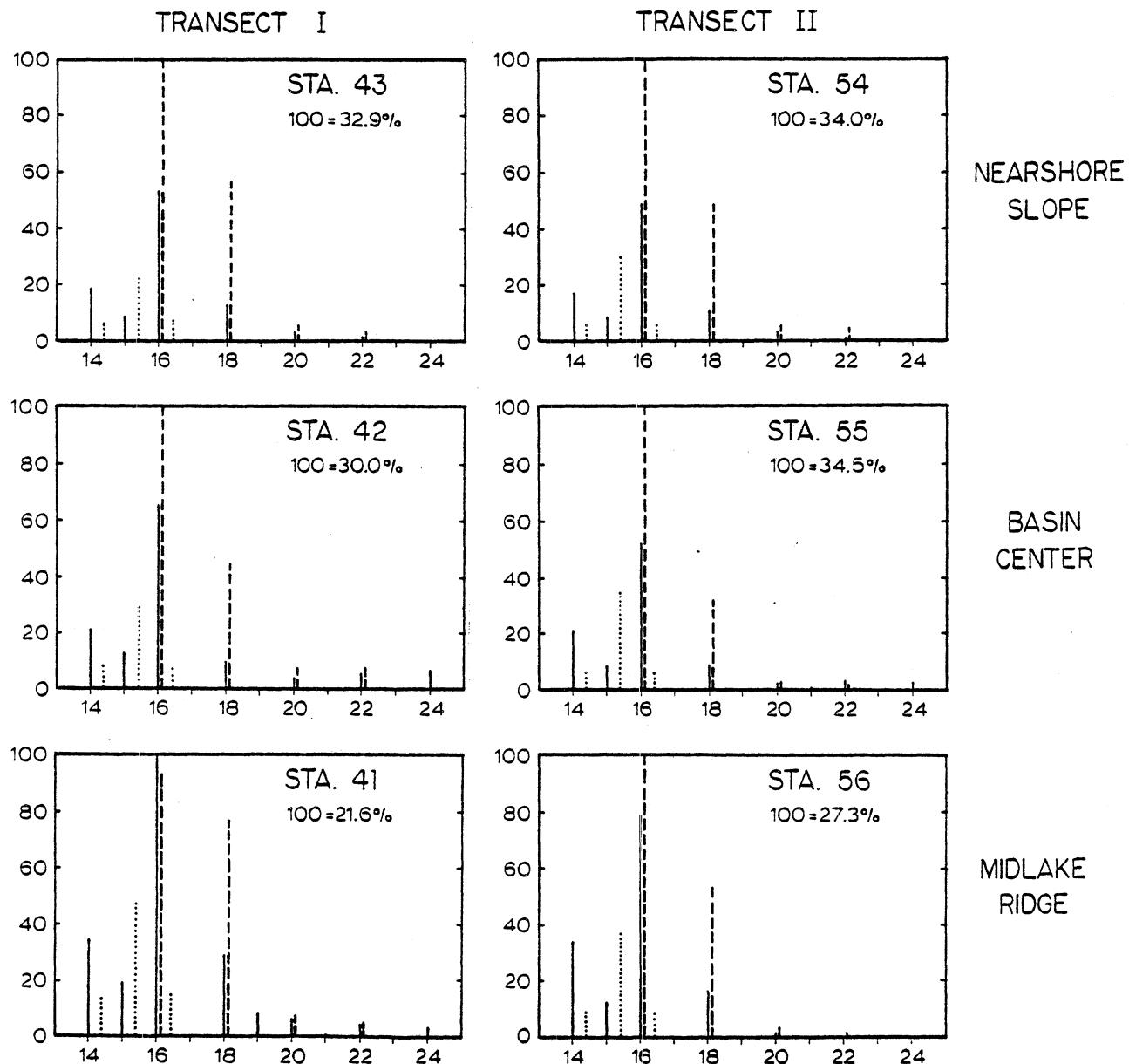


Figure 19. Distributions of fatty acids in surficial sediment samples from two transects across the Goderich Basin of southern Lake Huron. Distributions normalized to major component. Solid line = n-alkanoic acid, dashed line = n-alkenoic acid, dotted line = iso plus anteiso acid.

of saturated and unsaturated normal fatty acids with carbon chain-lengths of 14, 16, and 18. These distributions lack the large contribution of longer-chain n-alkanoic acids found by Cranwell (1974) and Brooks *et al.* (1976) in several English lakes. Such acids, from C₂₂ to C₂₈, are indicative of land-derived organic matter while C₁₂ to C₁₈ acids suggest aquatic sources (Cranwell, 1974). Indeed, the distributions found in the Lake Huron sediments resemble more closely fatty acid distributions reported by Cooper and Blumer (1968) and Farrington and Quinn (1973) for marine sediments than those described in English lakes. However, Matsuda and Koyama (1977) report a surficial sediment fatty distribution in Lake Suwa, Japan, which is very similar to the Lake Huron distributions shown in Figure 19. It is probable that the dominant fatty acid sources in Lake Huron, as well as in Lake Suwa and the marine locations, are aquatic.

The abundance of monounsaturated acids such as palmitoleic and oleic shown in Figure 19 gives support to an aquatic source of much of the acids in Lake Huron sediments. Palmitoleic acid has been found in relatively high levels in phytoplankton (Chuecas and Riley, 1969; Lewis, 1969; De Mort *et al.*, 1972; Boutry and Barbier, 1974) and accompanying relatively high concentrations of oleic acid in sediment bacteria (Johns *et al.*, 1977). In addition, the longer-chain C₂₂ unsaturated acid in the distributions in Figure 19 is docosahexaenoic acid and may indicate a contribution of zooplankton lipids.

Longer-chain n-alkanoic acids characteristic of terrigenous sources (Brown *et al.*, 1972; Cranwell, 1974, 1977; Gaskell *et al.*, 1975) are found, however, at stations 42 and 55 near the deepest parts of the Goderich Basin and at station 41 on the flank of a mid-lake subaqueous ridge. These acids could have been transported to the bottom of this basin associated with sediment articles originating from land run-off. Large amounts of n-alkanoic acids can be adsorbed by suspended sediments, and longer-chain acids are preferentially adsorbed relative to shorter-chain ones (Meyers and Quinn, 1973). Thus transport from terrigenous sources and accumulation in the basin center can be used to explain the saturated C₂₂ and C₂₄ acids found at stations 42 and 55, and it is reasonable to expect a similar although perhaps much smaller accumulation at most Lake Huron locations.

Station 41, however, is on the sloping side of a mid-lake ridge. The surficial sediment at this location is sandy and is probably a glacial till (Thomas *et al.*, 1973; Kemp *et al.*, 1974). Therefore, this sediment may be considerably older than that at any of the other locations in this study which appear to be accumulating modern sediments. Matsuda and Koyama (1977) have found an increase in abundance of C₂₄ relative to C₁₆ n-alkanoic acids which occurs with depth of burial in Lake Suwa sediments, suggesting preferential degradation of shorter-chain acids in sediments with time. It is possible that the presence of C₂₂ and C₂₄ saturated acids at station 41 is due to a loss of shorter-chain acids and an accompanying enhancement of the relative contribution of longer-chain acids over time. In support of this possibility, only at station 41 is the ratio of palmitoleic acid (16:1) to palmitic acid (16:0) less than unity (Table 3). The preferential loss of unsaturated acids over time of burial is well-documented (Parker, 1967; Farrington and Quinn, 1971a; Johnson and Calder, 1973; Farrington *et al.*, 1977; Sassen, 1977; Matsuda and Koyama, 1977). Hence, it is possible that the presence of longer-chain components in the n-alkanoic acid composition of this mid-lake station could be from diagenetic loss of shorter-chain compounds over time, rather than from modern transport and accumulation processes. However, it is also possible that

the relatively smaller contribution of alkenoic acids to total acids at station 41 indicates less biological productivity in this region of Lake Huron (Cranwell, 1977).

Branched-chain iso and anteiso fatty acids are important in the distributions shown in Figure 19. These lipids are abundant in sediment bacteria (Leo and Parker, 1966; Cooper and Blumer, 1968; Cranwell, 1973a, 1974; Johns *et al.*, 1977), and their presence is indicative of microbial biomass and alteration products in sediments (Parker, 1967; Boon *et al.*, 1975; Brooks *et al.*, 1977). In the two transects across the Goderich Basin, the proportion of iso plus anteiso C₁₄, C₁₅, C₁₆ acids increases with distance from shore, and the proportion of monounsaturated acids decreases (Figure 19). Johnson and Calder (1973) found that an increase of branched acids and a decrease in unsaturated acids with depth, or age of burial, in a marsh sediment was caused by *in situ* microbial activity. The distributions found in these Lake Huron samples may result from (1) different benthic environments having characteristic microbial populations across the transect, or (2) an increase in sediment transport time from land to each location and therefore in exposure to microbial alteration. While benthic environments probably are different, a progressive change such as seen in Figure 19 suggests distance from land may be an important factor in the geolipid content of these sediments. Furthermore, sedimentation rates decrease with distance from land in these transects (J. A. Robbins, personal communication, 1977), indicating the mean surficial sediment sample age increases across the basin. The location have the slowest accumulation rate and therefore greatest mean sample age is station 41, near mid-lake. This sample displayed the greatest amounts of branched fatty acids in Figure 19. Thus, analysis of these transect samples leads to the conclusion that slower sedimentation rates contribute to greater microbial alteration of fatty acids associated with accumulating sediment particles.

Figure 20 shows that distributions of n-alkanes in surficial sediments from Goderich Basin are bimodal. Shorter-chain alkanes (C₁₅ to C₁₉) comprise one part of these distributions, and longer-chain hydrocarbons (C₂₅ to C₃₃) the other. Shorter-chain alkanes, most prominently n-C₁₇, are indicative of algal hydrocarbons (Clark and Blumer, 1967; Winters *et al.*, 1969; Blumer *et al.*, 1971; Youngblood *et al.*, 1971; Giger and Schaffner, 1975; Paoletti *et al.*, 1976). Thus, there is an important input of algal hydrocarbons, probably from within Lake Huron, to these sediments. The longer-chain portions of the alkane distribution are dominated by C₂₅, C₂₇, or C₂₉ in the various samples. Higher plants typically have n-alkane maxima at C₂₇, C₂₉, or C₃₁ (Douglas and Eglington, 1966; Cranwell, 1973b; Giger and Schaffner, 1975) and exist as land or as emergent aquatic species. Freshwater zooplankton distributions commonly are from C₂₃ to C₂₇ peaking at C₂₅ (Giger and Schaffner, 1975). Combination of these two very likely sources would provide the longer-chain n-alkane distributions shown in Figure 20, and addition of an algal hydrocarbon component would give the overall patterns found in these sediments.

Although differences exist among the distributions in Figure 20, the similarity of all six is striking. Evidently, all n-alkanes added to the sediments of southern Lake Huron have common or very similar origins, even though concentrations both absolute and relative to total organic carbon decrease with distance from land (Tables 2 and 3). Differences in fatty acid distributions are found in these sediment samples (Figure 19) and are best explained by alteration of biological source materials. Therefore, the lack of differences in n-alkane distributions supports the general view of the more

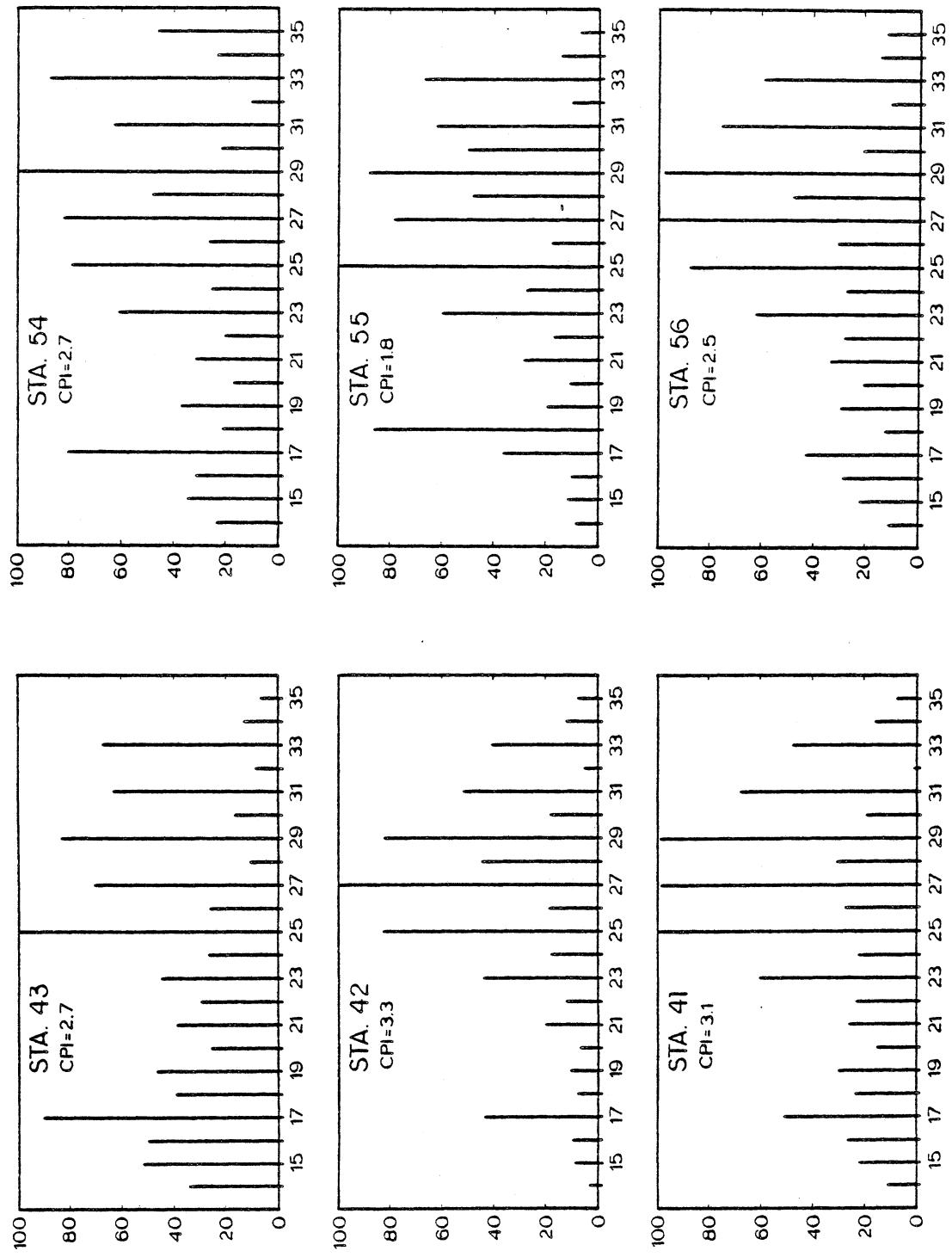


Figure 20. Distributions of n-alkanes in surficial sediment samples from two transects across the Goderich Basin of southern Lake Huron. Distributions normalized to major component.

refractory nature of hydrocarbons relative to acids.

It is interesting to compare the n-alkane distributions in Figure 20 to those found in other surficial sediments. The contribution of longer-chain components representative of a terrigenous input is less in these Lake Huron samples than in the sediments of Blelham Tarn, an oligotrophic English lake (Cranwell, 1973b), of Grasmere, a moderately productive English lake (Brooks, *et al.*, 1976), and of Lake Quinault, an oligotrophic lake in Washington, U.S.A. (Wakeham, 1976). Coastal marine sediments receiving large amounts of land-derived organic material have n-alkane distributions characterized by longer-chain components (Gaskell *et al.*, 1975; Gearing *et al.*, 1976; Brooks *et al.*, 1976), and contain proportionally more C₂₇-C₃₃ n-alkanes than do these Lake Huron sediments. Although not dominated by long-chain hydrocarbons, the n-alkane distributions are also not strongly skewed toward shorter components. The relative amounts of C15 to C19 n-alkanes is less than in sediments from Rostherne Mere in England (Brooks *et al.*, 1976), Lake Sammamish in the state of Washington (Wakeham, 1976), the Greifensee in Switzerland (Giger and Schaffner, 1975) and Mono Lake in California (Reed, 1977). These lakes, all eutrophic, have high algal populations and n-alkane distributions in their sediments which are dominated by n-heptadecane. Similar distributions have been reported for marine areas believed to be dominated by an algal source of organic matter (Gearing *et al.*, 1976; Palacas *et al.*, 1976).

Sediment n-alkane distributions of Goderich Basin most closely resemble those reported for Esthwaite Water in England (Brooks *et al.*, 1976) and Lake Washington (Wakeham and Carpenter, 1976). Both these lakes are highly productive and receive considerable runoff from their drainage basins. However, the Goderich Basin of southern Lake Huron is neither highly productive nor receives large amounts of runoff relative to its volume, resulting in lower absolute amounts of total organic carbon and geolipids in its sediments compared to these two lakes. It is interesting that these three lakes have such similar n-alkane distributions, evidently from similar proportions of input materials even though absolute concentrations differ. These proportions can change with time, as shown by Wakeham and Carpenter (1976) in Lake Washington where less productive aquatic conditions are recorded deeper in the sediment by a relative decrease in shorter-chain n-alkane contributions as well as decreases in concentrations of total aliphatic hydrocarbons and organic carbon.

Carbon preference indices (Cooper and Bray, 1963) of the six Goderich Basin samples are fairly high, reflecting large amounts of recently biosynthesized higher plant material in the n-alkane distributions. These values, between 1.8 and 3.3, are similar to those reported for uncontaminated modern sediments from both marine (Clark and Blumer, 1967) and freshwater environments (Cranwell, 1973b; Brooks *et al.*, 1976; Wakeham and Carpenter, 1976). Evidently, the large size of Lake Huron has protected this portion of it from demonstrable impacts of urbanization similar to those shown for Lake Washington (Wakeham and Carpenter, 1976; Wakeham, 1976, 1977a, 1977b) and Lake Zug (Giger *et al.*, 1974).

In surficial sediments from Saginaw Bay, concentrations of both n-alkanes and unsaturated hydrocarbons shown in Table 2 are about twice as high as in those of similar total organic carbon levels in the Goderich Basin (stations 42 and 55), yet fatty acid levels are comparable in both locations. Ratios of these geolipid components to total organic carbon reveal no strong trends within the Saginaw Bay sampling transect, although station 6A which is closest

to land has higher ratios than the other Saginaw Bay stations. These observations are consistent with the suggestion that n-alkanes may be to a large extent land-derived, because all locations within Saginaw Bay are influenced by land runoff via the Saginaw River (Figure 1). Furthermore, the data in Table 2 from Saginaw Bay are also consistent with the idea that unsaturated hydrocarbons are related to organic matter or sediment character rather than being from terrigenous sources because all the Saginaw Bay samples are similar to stations 42 and 55 in Goderich Basin in these parameters. However, the absence of enhanced fatty acid amounts expressed as either concentrations within the sediments or as ratios to organic carbon levels implies an additional source of both saturated and unsaturated hydrocarbons in Saginaw Bay. This may be from a combination of land runoff containing hydrocarbons and of different biological communities in the waters and sediments of the Bay as compared to the open lake.

The fatty acid distributions in Saginaw Bay sediments shown in Figure 21 are very similar to each other. Relative amounts of n-alkanoic acids are the same in stations 6A, 17A, and 30A and differ only due to the appearance of longer-chain acids in station 42A. The latter station is closest to the mouth of the Saginaw River (Figure 1) and undoubtedly receives more land-derived organic material than the other stations from this large river and its watershed. The ratio of palmitoleic to palmitic acid in the four samples is quite consistent (Table 3), further reflecting similar fatty acid compositions. Furthermore, the contribution of branched acids is virtually the same in all samples of bay sediment. These distributions differ from those in the open-lake samples (Figure 19) in having lower amounts of branched acids and in their uniformity.

As indicated by sediment texture descriptions and TOC concentrations in Table 2 and by the ratio of total fatty acids to TOC in Table 3, the sedimentary environment appears to be fairly uniform in Saginaw Bay. This is probably the result of sediment particle dispersion within this shallow and well-mixed bay. While surficial sediment grain size does vary in Saginaw Bay (Wood, 1964), the mean size distribution of the four locations sampled in this study is between 5.5 and 6.0 phi units (E. Seibel, personal communication, 1977). Lipid material can become strongly associated with suspended sediment particles (Meyers, 1972; Shaw, 1973), and thus processes causing transport and distribution of sediment particles will also disperse associated lipids such as fatty acids and hydrocarbons and contribute towards their uniform deposition.

Normal alkane patterns in the bay sediments are also affected by deposition of well-mixed sediments. As shown in Figure 22, the distributions at stations 6A, 17A, and 30A are very similar, and the distribution at station 42A is only slightly different. All locations have bimodal distributions maximized at C_{17} and at C_{27} or C_{29} . Contributions of C_{24} are less than in the open-lake sediment distributions in Figure 20, but amounts of C_{33} are high at both Saginaw Bay stations and near-shore Goderich Basin stations (43 and 54). Major sources of n-alkanes to the Saginaw Bay sediments appear to be algal and higher plant, with zooplankton contributing a smaller amount relative to the open-lake.

An unresolved envelope of aliphatic hydrocarbons underlying the resolved n-alkane peaks is present in large amounts in the Saginaw Bay surficial sediment hydrocarbons (Figure 3). The Saginaw Bay UCM's are comparable to one reported for Lake Sammamish sediments by Wakeham (1976), whereas in Goderich Basin sediments they are similar to one in pristine Lake Quinault. Because the

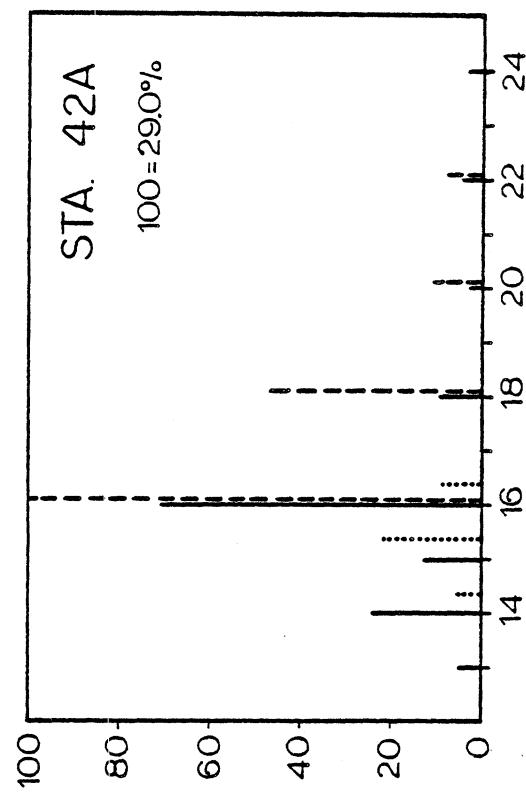
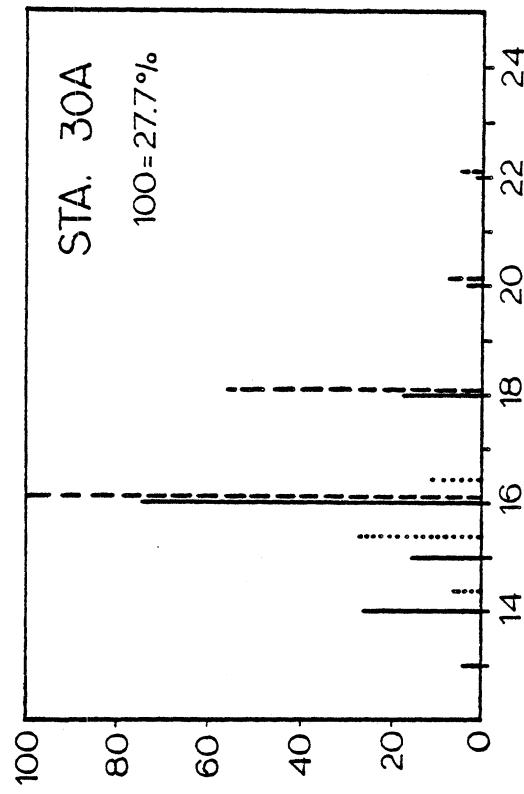
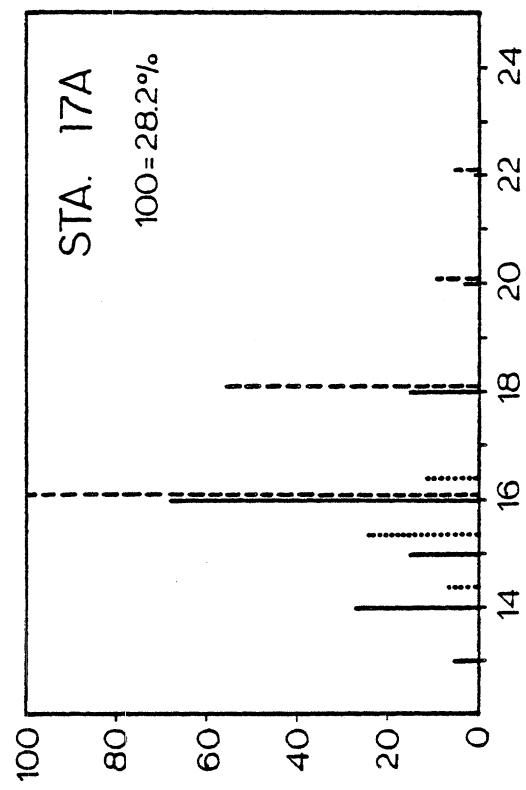
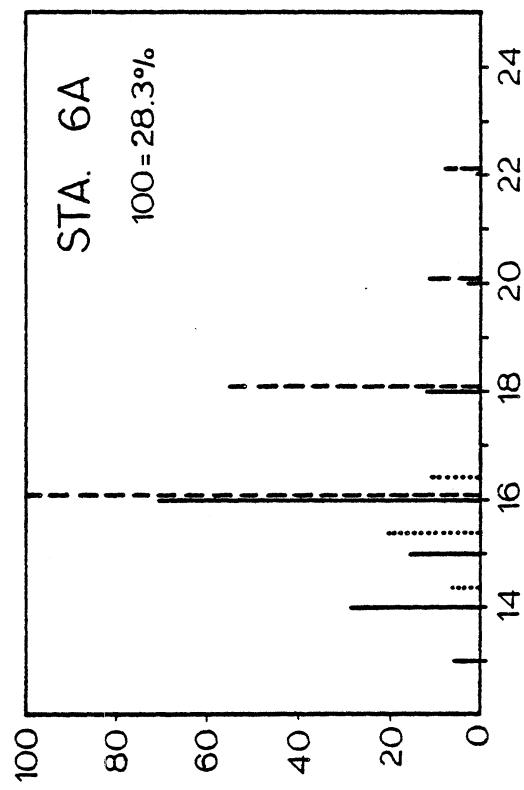


Figure 21. Distributions of fatty acids in surficial sediment samples from Saginaw Bay of Lake Huron.
See legend of Figure 19.

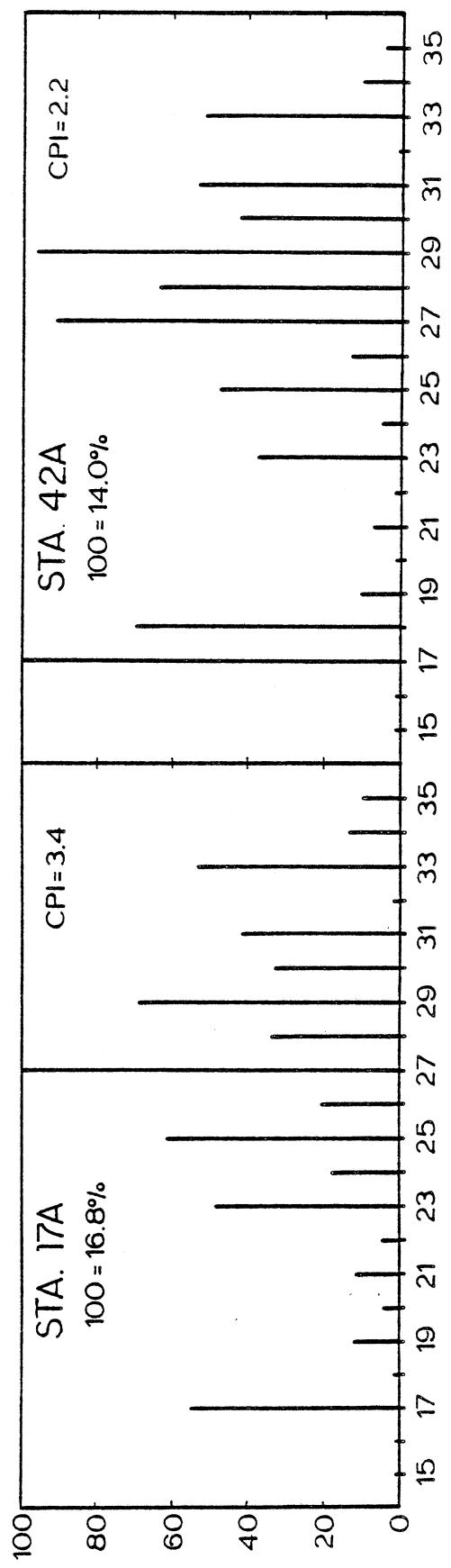
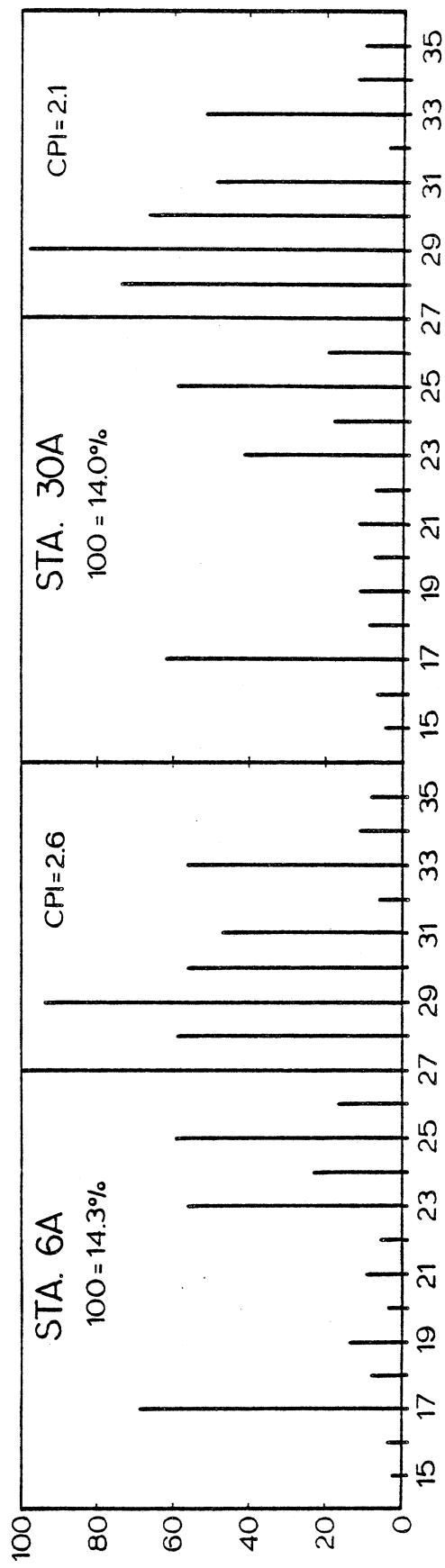


Figure 22. Distributions of n-alkanes in surficial sediment samples from Saginaw Bay of Lake Huron.
See legend of Figure 20.

presence of a UCM is considered diagnostic of petroleum contamination (Shaw, 1973; Palacas *et al.*, 1976; Gearing *et al.*, 1976; Wakeham, 1976, 1977a, 1977b; Wakeham and Carpenter, 1976; Farrington and Tripp, 1977), it is likely that Saginaw Bay sediments contain petroleum-derived hydrocarbons. These could be introduced into the bay by urban runoff from the industrial cities along the Saginaw River and its tributaries, and this possibility is consistent with the higher hydrocarbon-to-TOC ratios of bay sediments relative to Goderich Basin sediments in Table 3.

However, the bimodal distributions in Figure 22 strongly suggest a recent biological source of the n-alkanes in Saginaw Bay, and the CPI values of 2.1 to 3.4 are not as low as would be expected for weathered petroleum, for which these would be closer to unity. Evidently, the saturated hydrocarbons exist as a mixture of resolved, recently biosynthesized compounds and unresolved, weathered hydrocarbons. This is not surprising. It is probable that during weathering a preferential loss of resolved hydrocarbons occurred as shown by Bailey *et al.* (1973) for bacterial degradation of crude oil, leaving a UCM. In addition to petroleum hydrocarbons, it is possible that other sources, such as weathered hydrocarbons from erosion of geological formations, microbial synthesis, and industrial effluents, may have contributed to the hydrocarbon mixture in Saginaw Bay sediments.

SOUTHERN LAKE HURON CORES 74-12 AND 75-58

These cores both come from the Goderich Basin of Lake Huron, and they will be discussed together so that their contents can be compared. Core 74-12 originates from near the center of the basin. Its vertical profiles of total organic carbon and moisture content (Figure 4) combined with the absence of observable stratigraphic units indicate a continuous record of sedimentary history. According to ^{210}Pb data of J. A. Robbins (in preparation), the sedimentation rate is 1.1 mm/yr and the mixing depth is 4.0 cm for this core. Therefore, sediment at the bottom of this core was deposited about 450 years ago, and about 40 years of sedimentary record is averaged by mixing. Core 75-58 is from the eastern edge of the basin. Discontinuities in sediment accumulation are suggested by variations in total organic carbon and percent moisture content (Figure 10) which agree with observed stratigraphic units in this core. The sequence of sand (3-5 cm), brown clay (5-9 cm), gray clay containing pebbles (9 cm to bottom) is overlain by a sandy silt. The sandy layer is probably a diastem separating modern sediments from glaciolacustrine sediments (R. L. Thomas, personal communication). Therefore, sediments below a depth of 5 cm could be about 11,000 years old, and differences in organic constituents should exist between these two cores.

Comparison of concentrations of total unsaturated and aromatic hydrocarbons shown in Figures 5 and 11 shows that core 74-12 contains several times as much of these materials as does core 75-58. In the latter core, the highest level is at the surface, and the amount present drops to a low value by a depth of 6 to 7 cm and varies little below this. In contrast, core 74-12 has substantial increases in concentration at several depths in the core although these appear to be confined to the most recent 80 years of sediment accumulation. However, until better identifications of the components of this hydrocarbon fraction are available, interpretation of these distributional patterns would be too speculative to be attempted in this report.

Surface concentrations of total aliphatic hydrocarbons are similar at these two core locations (Figures 5 and 11). They are from 17 to 23 $\mu\text{gm/gm}$ as determined from the nonpolar SP-2100 column data. An overall general decrease in concentration is found in core 74-12, accompanied by considerable fluctuations and a concentration maximum at a depth of 7 to 8 cm. In contrast, total aliphatic hydrocarbon concentrations in core 75-58 decrease drastically from the surficial level to that found at a depth of 3 to 4 cm (Figure 11). Little variation is found beneath this depth, and values remain below 3 $\mu\text{gm/gm}$. The drastic decrease coincides with the sandy layer which is believed to represent an interruption of the sedimentary record. This layer also has the lowest level of total organic carbon found in core 75-58, so the low level of aliphatic hydrocarbons may result from an overall low amount of organic matter in general. Such a paucity of organics could be a reflection of the relative coarseness of the sediment particles comprising this stratigraphic unit. However, it is interesting that the amount of aliphatic hydrocarbons found below this layer remain low, even though the concentrations of total organic carbon climb to about three times that in the sandy layer (Figure 10). In other words, the contribution of aliphatic hydrocarbons to the total organic matter is less below this layer than in it or above it, and it is also less than in core 74-12.

Such a change in the contribution can occur through post-depositional alteration of organic materials in the sediments and also through variation in the nature of the source of the organic materials. There is evidence that both possibilities have had an effect upon the hydrocarbons found in core 75-58.

While the percentages of n-alkanes in the total aliphatic hydrocarbon fractions of both cores are similar and remain at or near 60 percent (Figures 6 and 12), there are important differences in the ratios of odd-to-even n-alkanes as expressed as the carbon preference index (CPI) of Cooper and Bray (1963). These values are lower in core 75-58 than in core 74-12.

Although these differences are not large, they are derived from a large number of individual measurements and show an unmistakable trend for a reduced odd-over-even predominance in the n-alkane composition of core 75-58. Similar trends have been documented in hydrocarbon composition found in sediment of increasing geologic age (e.g., Cooper and Bray, 1963). These have been interpreted as being the result of post-depositional alterations of hydrocarbons and hydrocarbon precursors in the sediments. Because much of core 75-58 is believed to be considerably older than the sediments in core 74-12 it is not inconsistent to expect to find evidence of diagenetic changes in the organic constituents of core 75-58, and the difference in CPI's may indicate this.

However, there is also evidence of differences in sources of the organic materials present in these two cores. Hydrocarbons in general and n-alkanes in particular can serve as indicators of the biological origins of organic matter. Histograms of n-alkane distributions derived from the polar SP-1000 column data of the two cores can reveal changes in hydrocarbon composition with depth which would imply variations in the makeup of the biological communities supplying organic materials to these sediments.

Distribution of n-alkanes from surficial sediments and three deeper sections of core 74-12 are shown in Figure 23. In the surficial distribution, n-C₂₇ is the dominant n-alkane, and substantial contributions of n-C₂₃ and n-C₂₅ exist. Giger and Schaffner (1975) found the dominant n-alkanes to be n-C₂₇ and n-C₂₉ in emergent aquatic plants and n-C₂₄ and n-C₂₅ in a mixed

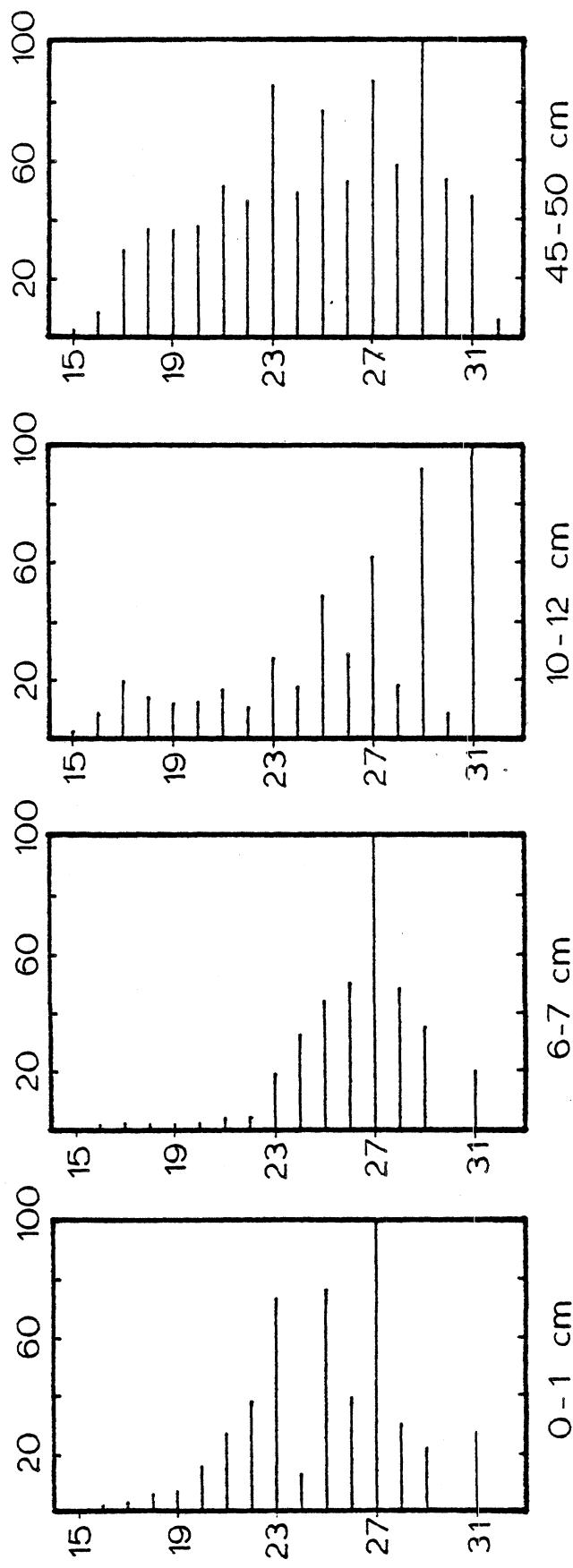


Figure 23. Histograms of n-alkane distributions at four depths in core SLH-74-12 from the Goderich Basin of southern Lake Huron. Distributions normalized to major component. Data obtained from polar SP1000 column data.

zooplankton sample from a Swiss lake. Therefore, the n-alkanes present in this sample may be from a mixture of higher plant and zooplankton-like sources.

In the sediment core sections from 6 to 7 cm and 10 to 12 cm, the contribution of zooplankton-type n-alkanes is small and possibly negligible. These distributions are dominated by longer chain n-alkanes characteristic of higher plants. At 10 to 12 cm, n-C₂₉ and n-C₃₁ are the major alkanes, and there is a fairly strong odd-over-even preference as indicated by the 3.3 CPI value. This type of distribution has been reported to be typical of hydrocarbons derived from watersheds in which grasslands are the major contributors of organic material (Cranwell, 1973b). The distribution found at 6 to 7 cm is dominated by n-C₂₇, more typical of aquatic grasses (Giger and Schaffner, 1975) or forests (Cranwell, 1973b). Therefore, the hydrocarbon distributions at these two depths may indicate periods which were 60 and 100 years, respectively, ago when zooplankton populations were lower and contribution of land-derived organic matter to the sediments was greater than at present. Furthermore, the difference in major alkanes between these two sections may also record a period of low forest cover in the drainage area serving the Goderich Basin about 100 years ago. Thus, these distributional patterns may be in part the effect of deforestation.

At the bottom of this core, the major n-alkanes are C₂₃, C₂₅, C₂₇, and C₂₉. The approximate age of this sediment section is 410 to 450 years. The hydrocarbon distribution suggests important contributions of organic materials derived from zooplankton and from forests at this time. Thus, variations in sources of organics are indicated by the n-alkane compositions of the sections of core 74-12. Such variations can influence the CPI calculated at each depth to some degree, so these latter values must be interpreted cautiously.

Differences in n-alkane composition similar to those in core 74-12 can also be seen in core 75-58 in Figure 24. Surficial sediment contains n-C₂₅ and n-C₂₇ as major components and a large amount of n-C₂₉. This distribution suggests a zooplankton-type source of organic matter as being most important, followed closely in importance by aquatic grasses or forests as sources. A large amount of n-C₁₇ is also present. This n-alkane is the major component of total hydrocarbon contents of a freshwater bluegreen alga (Giger and Schaffner, 1975) and of marine pelagic and benthic red algae (Blumer, *et al.*, 1971; Youngblood *et al.*, 1971). Consequently, the presence of this alkane may indicate an abundance of phytoplankton in surface lake waters and incorporation of some of their constituents in the underlying sediments. However, the surficial sediments of core 74-12 did not contain a large contribution of n-C₁₇. Both core locations are in the Goderich Basin and separated by only 6 km distance, an interesting contrast.

Possible explanations for the different surficial distributions in these two cores include major differences between types of organic matter incorporated in the sediments in 1974 and in 1975, large-scale changes in surface productivity from 1974 to 1975, and important differences in the benthic environments of these two areas. The first two possibilities are not likely to be important, mostly because bioturbation and mixing of surface sediments will usually average any one year's sediment accumulation with the accumulation of the previous 3 to 10 years (J. A. Robbins, *in preparation*). This would greatly diminish any annual differences in the nature of sedimented materials.

There could, however, be differences in the benthic environments of these locations. Although both sediment types are similar (Table 1), the site of

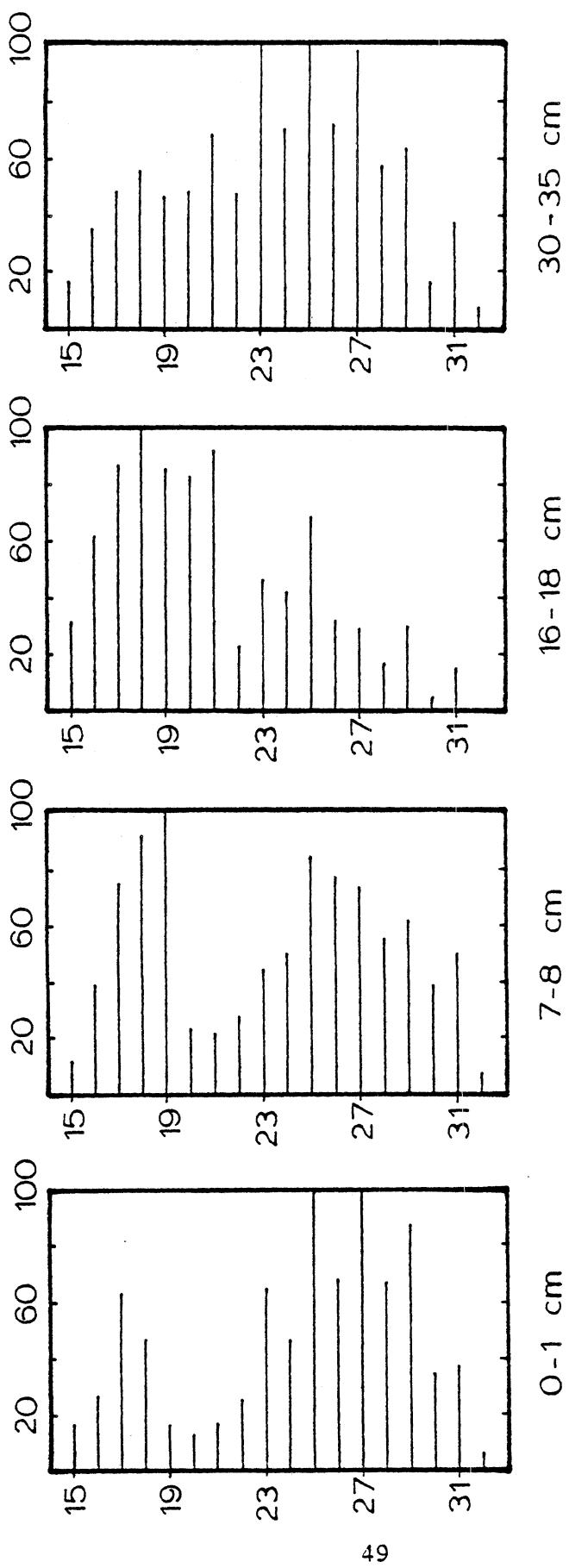


Figure 24. Histograms of n-alkane distributions at four depths in core from the Goderich Basin of southern Lake Huron. Distributions normalized to major component. Data obtained from polar SP1000 column data.

core 74-12 is deeper (91 m) than that of core 75-58 (73 m). This depth difference, combined with the subsurface sandy layer in core 75-58 could result in sufficient dissimilarity between the two locations to cause a distinction in their benthic populations. This, in turn, could be reflected in the hydrocarbon content of the sediments. While $n\text{-C}_{17}$ is the major hydrocarbon of red benthic algae, it is a minor component of brown benthic algae (Youngblood, *et al.*, 1971). Also, some bacteria have been shown to contain large amounts of $n\text{-C}_{17}$, while others do not (Albro, 1970). Therefore, it is quite possible that the differences in hydrocarbon compositions between the surficial layers of these two cores is due to the addition of hydrocarbons of a benthic origin in core 75-58 to those obtained from zooplankton and land runoff. In support of this theory, higher levels of aliphatic hydrocarbons are found in the surficial layer of core 75-58 than of core 74-12.

The contribution of shorter-chain-length n -alkanes is large through core 75-58, indicating the importance of algal or bacterial biomass as sources of organic matter in this core. The histograms of n -alkanes from the 6 to 7 cm and 16 to 18 cm sections (Figure 24) have particularly large components of hydrocarbons in the C_{16} to C_{21} range, and all of the histograms show a relatively large amount of $n\text{-C}_{25}$. This is the major n -alkane in the surficial and 30 to 35 cm sections. Furthermore, the odd-to-even predominance, or CPI, is low in these histograms. The combination of abundance of $n\text{-C}_{25}$ and low CPI was found by Giger and Schaffner (1975) to be representative of mixed lacustrine zooplankton hydrocarbons. Therefore, the n -alkanes in core 75-58 could record a predominantly algal and zooplankton source of organic matter to this sediment.

However, because the sediment below the sandy layer is thought to be glaciolacustrine material approximately 11,000 years old, the differences between the n -alkanes in this core and those in core 74-12 could also be due to postdepositional alteration. Such diagenetic changes would include both chain-shortening of hydrocarbons and reduction in the CPI. While the observed distributions may result in part from such changes, the presence of two fairly distinct groupings of n -alkanes in sections 6 to 7 cm and 16 to 18 cm and the higher CPI in the oldest, bottom section than in either of the two above speak against diagenesis of hydrocarbons being important. Instead, it is probable that aliphatic hydrocarbons reflect their biological sources for at least the first 11,000 years of their burial in Great Lakes Sediments.

In contrast to aliphatic hydrocarbons, fatty acids appear to be relatively quickly degraded in these sediments. The concentration of total fatty acids drops from about 140 $\mu\text{gm/gm}$ in surficial sediments of core 74-12 to less than half this value at a depth of 10 to 12 cm (Figure 7). Other workers have reported considerable alteration or destruction of fatty acids in both marine sediments (Rhead *et al.*, 1971; Farrington and Quinn, 1971a, Boon *et al.*, 1975; Johnson and Calder, 1973; Farrington *et al.*, 1977) and in freshwater sediments (Cranwell, 1974; Matsuda and Koyama, 1977). In this core, much of the reduction in concentration occurs in the 4 or 5 cm immediately below the zone of mixing which exists to a depth of about 4 cm (J. A. Robbins, in preparation). This can be interpreted to mean that, within the bioturbated region of sediment, fatty acids are being added by benthic organisms at a rate equal to or somewhat greater than the rate of destruction or alteration. Below the bioturbated zone, which usually marks the limit of oxygenated interstitial waters, addition of fatty acids is minimal, and removal processes dominate until a stable level of fatty acids is attained.

Such an explanation would imply that benthic sources of fatty acids are very important to the total concentration. This is probably true and has been suggested for marine sediments (Boon *et al.*, 1975). However, some reports indicate that multiple sources of fatty acids can be identified in lacustrine sediments (Cranwell, 1974; Brooks, *et al.*, 1976). While the fatty acid distributions in core 74-12 may be influenced somewhat by alternate sources, little indication can be found for major changes in source material.

As total fatty acid concentrations decrease with depth in the top 10 to 12 cm, the relative amounts of unsaturated acids decrease faster than those of saturated acids (Figure 8). During this reduction in concentration, the relative proportions within both the saturated and unsaturated fatty acid classes remain nearly the same, as indicated by the histograms in Figure 9. This would not occur if differing biological sources were involved. This pattern would, however, occur if there were one dominant source which provided fatty acids which were then acted upon by nonbiological diagenetic mechanisms. Because most of the loss in fatty acids takes place in anoxic sediments, oxidation is not a likely mechanism. Instead, it is probable that these materials are incorporated into humic substances from which they are not easily extracted, inasmuch as fatty acids have been shown to be major components of humic and fulvic acids (Schnitzer, 1976).

SAGINAW BAY, CORE 75-30A

The hydrocarbon composition of Saginaw Bay sediments is unlike that of either of the Goderich Basin locations. The concentration of total resolved aliphatic hydrocarbons is twice as high in surficial sediments and drops to levels comparable to those in SLH 74-12 by a depth of 35 cm. This pattern suggests an increasingly enhanced input of hydrocarbons into Saginaw Bay during the last one hundred years. Over this period, the nature of hydrocarbons incorporated into the sediments also appears to have changed. The contribution of n-alkanes to total aliphatic hydrocarbons is diminished above 35 cm, and the CPI of the n-alkanes also decreases at 35 cm, although it reaches its highest value near the surface. A low CPI ratio is commonly found in petroleum-derived hydrocarbons and is usually accompanied by an increase in n-alkane content. Furthermore, n-alkane distributions generally shift to shorter chain lengths in petroleum. As shown in Figure 25, n-alkane distributions in this core do not shift toward shorter components near the surface. Therefore, a significant input of petroleum-type n-alkanes to this sediment is not indicated.

A more likely cause for the observed increase in aliphatic hydrocarbon content is from algal input. In each of the histograms in Figure 25, n-C₁₇ is present and is probably algal in origin. This component is greater nearer the surface than at the bottom of the core. Several reports of a low CPI in benthic bacteria and algae are discussed by Brooks *et al.*, (1976) which further supports a possible algal source. Finally, microbial activity is known to contribute branched fatty acids to sediments (Parker, 1967; Cooper and Blumer, 1968). It is probable that branched hydrocarbons can be derived from these acids, thus reducing the contribution of n-alkanes to the total hydrocarbons. The changes observed in the resolved aliphatic hydrocarbons in this core may be due to a larger input of these compounds from increasing phytoplankton populations combined with increasing benthic microbial densities. Therefore, these changes may reflect the cultural eutrophication of the waters overlying

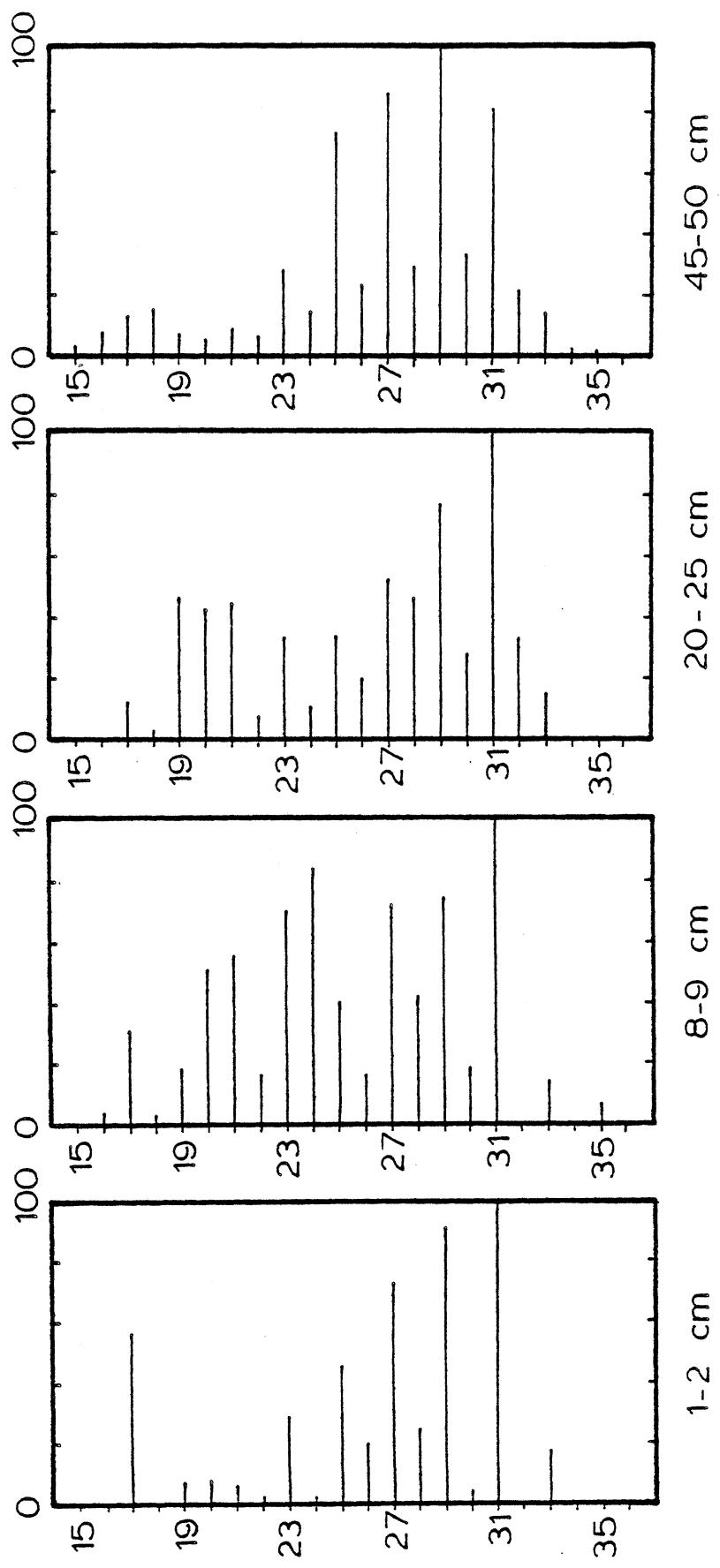


Figure 25. Histograms of n-alkane distributions at four depths in core SB-75-30A from Saginaw Bay of Lake Huron. Distributions normalized to major component. Data obtained from nonpolar SP2100 column data.

these Saginaw Bay sediments which increased over the last century (Beeton, 1969).

The patterns of total fatty acid concentration and contribution of unsaturated acids to the total showed decreases with depth as reported by other workers for a variety of marine and freshwater locations (Parker, 1967; Farrington and Quinn, 1971a; Brown *et al.*, 1973; Farrington *et al.*, 1977; Matsuda and Koyama, 1977; Matsuda, 1978). As shown in Figure 16, concentrations of acids with carbon chain lengths longer than C_{20} do not decrease appreciably with depth, although shorter-chain acid concentrations become smaller. Similar results have been found in Lake Suwa in Japan by Matsuda and Koyama (1977) and have been interpreted by these authors to be due to differences in relative rates of fatty acid degradation within the sediments. They conclude that shorter-chain and unsaturated acids are more quickly attacked by microbial agents and removed from sediments than are the longer-chain acids. While the rapid disappearance of unsaturated acids has been demonstrated by Rhead *et al.* (1971) and Rhead *et al.* (1972), selective attack by microorganisms on the basis of fatty acid chain length remains difficult to envision for saturated acids.

Instead of indicating selective degradation, the patterns in Figure 16 may record changes in the sources of fatty acids over time. Cranwell (1974) has proposed that acids of chain lengths from C_{12} to C_{18} are from aquatic algae and those of lengths from C_{22} to C_{28} are from higher land plants. Further differences between aquatic and land plants may exist. Cranwell (1977) has shown that branched alkanoic acids and normal unsaturated acids are characteristics of aquatic, but not land, sources. Hence, variations in relative abundances of these types of acids can indicate changes in the relative contributions of autochthonous, aquatic-derived organic matter and of allochthonous, land-derived material. Such changes could be the result of shifts in the oligotrophic or eutrophic status of a water body.

In the case of Saginaw Bay, core SB 75-30A contains higher amounts of both shorter-chain acids and unsaturated acids near the surface than below a sediment depth of 35 cm. If the presence of these compounds is diagnostic of increased algal input of organic matter, then a record of increasing eutrophication of Saginaw Bay is present in sediment deposited since about 1835. In view of evidence in hydrocarbon data leading independently to the same conclusion, this is probably a valid conclusion and is further supported by higher TOC values in surface sediments (Figure 13).

A major difference between the core from Saginaw Bay and the two Goderich Basin cores is the presence of a large, unresolved complex mixture in the aliphatic hydrocarbon fraction of core SB 75-30A. This mixture, present as a hump underlying the resolved peaks in Figure 18, decreases with depth in this core, but most rapidly around 25 to 30 cm. This coincides with the zone where the concentration of resolved aliphatic hydrocarbons becomes similar to that in core SLH 74-12. Thus, the appearances of the unresolved complex mixture and of enhanced aliphatic hydrocarbon concentrations correlate with each other.

The presence of an unresolved complex mixture of aliphatic hydrocarbons has been interpreted as being indicative of petroleum contamination (Shaw, 1973; Palacas *et al.*, 1976; Gearing *et al.*, 1976; Wakeham, 1976, 1977a, 1977b; Wakeham and Carpenter, 1976; Farrington and Tripp, 1977). The UCM present in the Saginaw Bay core decreases with depth similar to patterns found in Lake Washington by Wakeham (1976) and in coastal marine sediments by Farrington *et al.* (1977). These patterns have been interpreted to be the result of an

anthropogenic input of petroleum-derived hydrocarbons into the drainage area supplying water and water-borne sediments to the basins from which the cores originated. The change with depth suggests a high level of input in modern times and reflects the effects of urbanization upon water quality, since little or no UCM is found at sediment depths corresponding to pre-urbanization periods. Further evidence in support of the UCM found in Saginaw Bay sediments to be of a petroleum origin is given by the gas chromatograph--mass spectrometer data. The unresolved envelope is 86 percent cyclic hydrocarbons. These compounds are rare in organisms, but are abundant in petroleum (Farrington and Meyers, 1975). Hence, it appears likely that an anthropogenic loading of petroleum residues has been introduced to Saginaw Bay during the past 100 years, but a comparable process has not occurred to the Goderich Basin portion of southern Lake Huron.

In view of the depth-related changes in total organic carbon (Figure 13), hydrocarbons (Figures 14, 15, and 18), and fatty acids (Figures 16 and 17), it is interesting that the carbon isotope values show no change in this core. The ^{13}C values remain about -26.7 per mille. This is representative of biogenic organic matter having atmospheric CO_2 as a photosynthetic carbon source, suggesting a predominance of land-derived organic matter in Saginaw Bay sediments. It is possible that fatty acids and hydrocarbons, which comprise only a few percent of the total organic carbon, may not always be dependable indicators of the sources of all the organic constituents in subaqueous sediments.

SECTION 6

SUMMARY

Sediment samples were obtained at eight locations in the Goderich Basin of southern Lake Huron and four locations in Saginaw Bay (Figure 1). Two transects across the Goderich Basin yielded six surficial sediment samples, while two cores from this basin provided forty more. The bottom samples from one of these cores represented sediment deposited approximately 450 years ago. In the other core, bottom samples came from below an apparent interruption in sediment accumulation and are probably 11,000 years old. From Saginaw Bay, three surficial sediment samples were obtained from a transect of the bay, and twenty-three more from a core taken along this transect. The estimated age of the deepest sediment in this core is approximately 250 years.

The concentration of total organic carbon and of fatty acids, saturated hydrocarbons, and unsaturated hydrocarbons were measured in these samples as clues to variations in the input of organic materials to southern Lake Huron sediments over the past few hundred years. Further characterization of fatty acids and hydrocarbons was accomplished to provide information about the nature of the dominant sources of organic material. Three major sources were identified: autochthonous planktonic populations, autochthonous benthic populations, and allochthonous watershed sources. In addition, evidence of time-related changes in the character of each of these major sources is preserved in the sediments of Lake Huron.

Straight-chain saturated hydrocarbons were the best indicators of sediment organic matter sources in this study. Variations in the concentrations of these hydrocarbons and in their chain-length distributions provided information about both the abundance and type of organisms living in and near Lake Huron over the past few centuries. Analysis of fatty acids provided additional information, even though most of these geolipids appear to be derived from benthic populations and are subject to alteration processes soon after burial. It is probable that more sophisticated analysis of unsaturated and aromatic hydrocarbons and of sterols and other fatty alcohols could identify specific sources of organic materials in more detail. This is recommended for future investigations.

Decreases in the contributions of saturated hydrocarbons and fatty acids to total organic matter as distance from land increases in samples from the two transects across the Goderich Basin indicate the importance of land-derived geolipids in these sediments. Unsaturated hydrocarbon concentrations seem to be related more to the texture of the sediment than to its location, suggesting a primarily benthic source. Changes in concentration of these geolipid components with depth in sediment cores from the Goderich Basin indicate changes in relative importance of the three major sources of organic materials to this basin over the periods of time these cores represent. Similar changes are found in a sediment core from Saginaw Bay, and these correlate with

deforestation of the bay watershed from 1860 to 1880 and eutrophication of surface waters beginning about 1940. Indications were found of changes in organic constituents of sediments which appear to be caused by man-induced alterations of the Great Lakes ecosystem; signs of modern inputs of geologically old hydrocarbons could be detected. Thus, the changes in geolipid content of Lake Huron sediments identified in this study are probably due to changes in biological populations as well as to petroleum hydrocarbon contamination in some locations. Furthermore, indications are preserved in Lake Huron sediments that variations in biological populations occurred prior to European settlement of the lake watershed and thus can be natural periodic events.

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APPENDIX I

Lake Huron sediment samples not analyzed in this study. Prefix SLH indicates southern Lake Huron; SB indicates Saginaw Bay.

Station	Latitude-Longitude	Collection Date	Type
SLH - 3*	43°30'N - 82°00'W	10-3-74	core
SLH - 11	43°50'N - 82°17'W	10-3-74	core
SLH - 14A	43°55'N - 82°07'W	8-26-75	surficial
SLH - 18A	44°00'N - 82°00'W	8-27-75	core
SLH - 19*	44°05'N - 82°25'W	10-3-74	core
SLH - 21*	44°10'N - 82°15'W	10-3-74	core
SLH - 31	43°35'N - 82°20'W	10-3-74	core
SLH - 36	43°25'N - 82°00'W	10-3-74	core
SLH - 37	43°15'N - 82°07'W	8-24-75	surficial
SLH - 38	43°20'N - 81°55'W	8-24-75	surficial
SLH - 39	43°20'N - 82°00'W	8-24-75	surficial
SLH - 40	43°22'N - 82°02'W	8-24-75	surficial
SLH - 45	43°30'N - 81°50'W	8-25-75	surficial
SLH - 46	43°30'N - 81°55'W	8-25-75	core
SLH - 47+	43°30'N - 82°05'W	8-25-75	surficial
SLH - 50	43°35'N - 82°55'W	8-25-75	surficial
SLH - 51	43°35'N - 81°50'W	8-25-75	surficial
SLH - 52	43°40'N - 81°50'W	8-25-75	surficial
SLH - 53+	43°40'N - 82°00'W	8-25-75	surficial
SLH - 57	43°50'N - 82°10'W	8-26-75	surficial
SLH - 59	43°55'N - 82°10'W	8-26-75	surficial
SLH - 60+	43°55'N - 82°00'W	8-26-75	surficial
SLH - 61	43°55'N - 81°55'W	8-27-75	surficial
SLH - 62	44°00'N - 81°55'W	8-27-75	surficial
SLH - 63+	44°00'N - 82°05'W	8-28-75	surficial
SLH - 65	44°05'N - 82°10'W	8-28-75	surficial
SLH - 66+	44°05'N - 82°05'W	8-27-75	surficial
SLH - 67+	44°05'N - 82°00'W	8-27-75	surficial
SLH - 68	44°10'N - 82°10'W	8-28-75	surficial
SLH - 69	44°15'N - 82°10'W	8-28-75	surficial
SLH - 70	44°15'N - 82°20'W	8-28-75	surficial
SLH - 71	44°15'N - 82°50'W	8-28-75	surficial
SLH - 73	44°15'N - 83°00'W	8-28-75	surficial
SB - 7	43°58'N - 83°36'W	8-29-75	core
SB - 5A	43°58'N - 83°38'W	8-29-75	surficial
SB - 11A	43°56'N - 83°41'W	8-29-75	surficial
SB - 15A	43°54'N - 83°45'W	8-29-75	surficial
SB - 28A	43°51'N - 83°48'W	8-29-75	surficial

(continued)

APPENDIX I (continued)

Station	Latitude-Longitude	Collection Date	Type
SB - 44A	43°47'N - 83°41'W	8-29-74	surficial
SB - 50A	43°45'N - 83°43'W	8-29-75	surficial

*Transferred to D. K. Rea (Department of Atmospheric and Oceanic Science, The University of Michigan) for studies of grain size, texture, and mineralogy.

+Transferred to E. Vogler (Department of Chemistry, Indiana University) for studies of stable carbon isotope ratios in geolipid components of organic matter.

